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(54) Title: IONIZATION RADIATION IMAGEABLE PHOTOPOLYMER COMPOSITIONS		
(57) Abstract This invention discloses compositions that can be polymerized/crosslinked imagewise upon exposure to ionization radiation such as x-ray, electron beam, ion beam, and gamma-ray. This invention also discloses methods of use for these compositions for microfabrication of ceramics, for stereolithography, and for x-ray, e-beam, and ion-beam lithography which can be used for photoresists.		

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TITLE
IONIZATION RADIATION IMAGEABLE
PHOTOPOLYMER COMPOSITIONS
FIELD OF THE INVENTION

5 This invention discloses compositions consisting essentially of
(1) reactive monomer, (2) multi-functional cross-linking agent, and at least
(3) radiation sensitizer, (4) polymer binder, or (5) filler (with binder) that can be
polymerized/cross-linked imagewise upon exposure to ionizing radiation, such as
x-ray, electron beam, ion beam, and gamma-ray. This invention also discloses
10 methods of using these compositions for microfabrication of ceramics, for
stereolithography and as photoresist in x-ray, e-beam, and ion-beam lithography.

BACKGROUND OF THE INVENTION

UV-VIS-IR-sensitive photopolymer compositions have been used
extensively in many applications in the area of photolithography, graphic art,
15 stereolithography, and printing and publishing. All of these applications require
materials that can be polymerized imagewise; that is, the polymerization reaction
is spatially confined to the region irradiated by the photons to retain the input
image with good fidelity and spatial resolution. Because of the short penetration
depth (in absorbing media) and scattering problems of optical photons, the use of
20 relatively thin and transparent photopolymer films is usually required for these
applications. Opaque medium is very problematic for this technology. For
example, conventional photopolymer technology is not suitable for the patterning
of ceramic materials.

These issues may be resolved by the development of useful x-ray sensitive
25 photopolymers. X-ray has deeper penetration depth and, in the case of
lithography, can achieve better spatial resolution than optical based technique.
Unfortunately, no material has been developed that can be polymerized imagewise
by a relatively low intensity x-ray beam within a reasonably short duration, as best
known to the inventor. Organics have very low x-ray absorption efficiency and
30 polymerization reaction, if can be initiated by x-rays, tends to be inefficient and
requires the use of either very long exposure time or high power x-ray source,
such as synchrotron radiation. In addition, for applications requiring spatial
resolution, the polymerization reaction has to be spatially confined to the
irradiated region.

35 There are many potential applications for x-ray sensitive photopolymers if
these materials are available. The microfabrication of ceramics and metals (for
example, barrier rib fabrication for plasma flat panel display; S. W. Depp and
W.E. Howard, Sci. Amer. 260,40 March 1993), stereolithography (3D-solid object

modeling) (D.C. Neckers, Chemtech, October issue, p. 615, 1990) and photoresist for x-ray or e-beam or ion beam lithography (C. Grant Wilson in Introduction to Microlithography, eds. L.F. Thompson, C.G. Wilson, and M.J. Bowden, 1994, American Chemical Society, Chapter 3, p.139) are just a few examples. Other applications include x-ray contact microscopy (Applied Physics Letters, 72, 258 (1998) by A. C. Cefalas, P. Argitis, Z. Kollia, E. Sarantopoulou, T. W. Ford, A. D. Stead, A. Marranca, C. N. Danson, J. Knott, and D. Neely) and the fabrication of photonic crystals with photonic band gap properties (Science, 281, 802 (1998), by J. E. G. J. Wijnhoven and W. L. Vos).

10 The basic principles of initiating chemical reactions with ionization radiation can be found in "Radiation Chemistry" by A. J. Swallow, Wiley, 1973; and "Pulse Radiolysis" by M. S. Matheson and L. M. Dorfman, MIT Press, 1969. Here ionization radiation is defined to include x-rays, γ -rays, neutrons, charged particles (ion beam), and electron beam. The irradiation of matters with ionization radiation can generate excited states, free radicals, cations, and anions. Under the proper conditions, these reactive species can initiate chemical reactions such as polymerization, cross-linking, and bond breaking.

Several patents disclose the use of gamma ray radiation for industrial applications. U.S. 3,950,238 (April 13, 1976, R. J. Eldred) discloses an acrylonitrile-butadiene elastomer composition that can be cured by an electron beam. U.S. 4,004,997 (January 25, 1977, Tsukamoto, Matsumura, Sano) discloses a process of curing a resin filled with powdery ferromagnetic substance using radioactive rays. U.S. 4,303,696 (December 1, 1981, Brack) describes a method of curing a liquid prepolymer composition to form a waxy, release coating on a solid surface. U.S. 4,319,942 (March 16, 1982, W. Brenner) discloses electron beam curing of adhesive compositions containing elastomers for building flocked composite structures. U.S. 4,353,961 (October 12, 1982, Gotcher, Germeraad) discloses radiation cross-linking of fluorocarbon polymer to improve the mechanical strength. U.S. 4,547,204 (October 15, 1985, Caul) discloses resin compositions, such as acrylated epoxy and phenolic resin, which can be cured by electron beam for coated abrasive application. U.S. 5,098,982 (March 24, 1992, Long) discloses that the hardness of thermoplastic polyurethanes can be improved upon irradiation by electron beam. U.S. 5,037,667 (August 6, 1991, Dubrow, Dittmer) discloses that certain organopolysiloxanes can be grafted to polymeric supports by the irradiation with electron beams. U.S. 5,332,769 (July 26, 1994, Kakimoto, Eguchi, Kobayashi, Nishimoto, Iseki, Maruyama) discloses electron beam curing of adhesives for adhesion between a polyester film and a metal plate. J. Polym. Sci., XLIV, 117-127(1960) by B. Baysal, G. Adler, D. Ballantine, and

P. Colombo discloses solid state polymerization of acrylamide initiated by gamma ray radiation to produce polyacrylamide. There was not enough solubility differentiation between the starting material and the product to allow spatially defined image formation. U.S. 4,115,339 (September 19, 1978, by A. J. Restaino) discloses gamma ray initiated polymerization of nitrogen-containing vinyl monomers to form aqueous gels of water-soluble polymers. Both the starting material and the product are water-soluble so spatially defined image formation cannot be achieved.

All of the above patents and papers disclose methods or compositions used mostly for coating and adhesion applications under gamma ray radiation. The efficiency was generally low and the required spatial resolution for imaging applications was not demonstrated.

Recently, synchrotron radiation has been used to cross link polymethylmethacrylate for the precision machining of solid parts (Johnson, Milne, Siddons, Guckel, Klein, Synchrotron Radiation News, 9, 10 (1996)). The intensity of synchrotron radiation is roughly 1 million times higher than the common laboratory x-ray machines such as the ones used in this work. The extremely high intensity of the synchrotron radiation means the polymerization/cross-linking reactions can be initiated from almost any compositions (that is, it is non-discriminate). The high intensity also presents damage and heating problems with the mask that needs to be used for imaging applications. Because of the cost of the synchrotron machine and the limited availability, the use of synchrotron radiation is not practical. The compositions disclosed in this invention allow the use of commonly available, low intensity x-ray machine (or e-beam and gamma ray) to achieve spatially defined polymerization/cross-linking reactions.

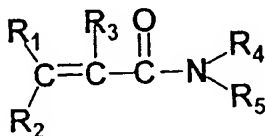
U.S. 5,556,716 (Herron and Wang) discloses x-ray sensitive photoconductive compositions for digital radiography applications. The compositions comprise of hybrids of organic polymers and inorganic nanoparticles. Unlike the materials disclosed in the present invention, x-ray generated electrons and holes in these photoconductors do not induce any chemical reactions; they are separated and transported out of the film under high fields.

SUMMARY OF THE INVENTION

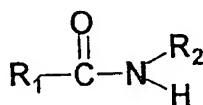
This invention discloses compositions that can be polymerized/cross-linked imagewise upon exposure to ionizing radiation such as x-ray, electron beam, ion beam, and gamma ray.

One of the disclosures of this invention is a composition, that can be polymerized/cross-linked imagewise by ionization radiation, consisting essentially of:

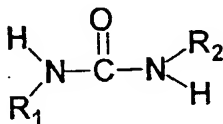
(A) from 10 to 90 weight percent of a reactive monomer having at least one amide functional group, said monomer selected from the group consisting of:



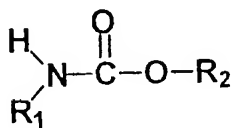
- 5 where R_1 , R_2 , R_3 , R_4 , and R_5 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, and aliphatic groups with $R'O-$ substituent where R' represents aliphatic group,
- 10 C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);



- 15 where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and acetamide;



- 20 where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20);



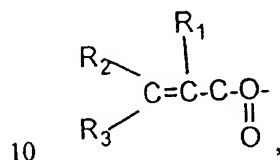
- 25 where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and amino-substituted aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

- 30 (B) from 10 to 90 weight percent of a multifunctional cross-linking agent, said cross-linking agent consists of a backbone with at least 2 functional groups, said backbone is selected from group consisting of:

- (1) linear or branched aliphatic chains, $-(\text{CRH})_n-$, $n=1-1000$, where R represents an aliphatic group, $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$ ($n=1$ to 20);
- (2) ethylene glycol chains, $-(\text{CH}_2\text{CH}_2\text{O})_n-$ where $n=1-1000$;
- (3) propylene glycol chains, $-(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_n-$ where $n=1-1000$;
- (4) cyclohexyl; and
- (5) isocyanurate, $\text{C}_3\text{N}_3\text{O}_3$; and

wherein the functional groups are selected from the group consisting of:

(a) acrylates,

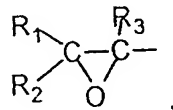


where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and aliphatic groups, $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$ ($n=1$ to 20);

(b) carboxylic acid, $-\text{COOH}$;

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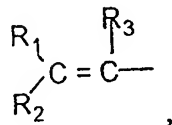
(c) epoxides,



where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, $\text{C}_n\text{H}_{2n+1}$

20 and $\text{C}_n\text{H}_{2n-1}$ ($n=1$ to 20); and

(d) vinyls,



25 where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$ ($n=1$ to 20); and

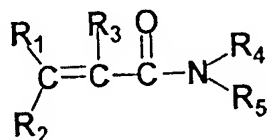
(C) from 0.1 to 80 weight percent of an inorganic radiation sensitizer

having a particle size in the range of 1 nanometer to 1000 nanometers, said radiation sensitizer is selected from the group consisting of VB-VIB

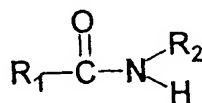
30 { semiconductors, VB-VIIB semiconductors, IIB-VIB semiconductors, IIB-VB semiconductors, IIIB-VB semiconductors, IIIB-VIB semiconductors, IB-VIB semiconductors, and IVB-VIIB semiconductors.

This invention also discloses a composition, that can be polymerized/cross-linked imagewise by ionization radiation, consisting essentially of:

- (A) from 10 to 90 weight percent of a reactive monomer having at least one amide functional group, said monomer selected from the group consisting of:



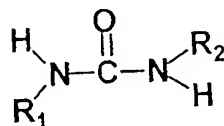
- where R_1 , R_2 , R_3 , R_4 , and R_5 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, and aliphatic groups with $R'O-$ substituent where R' represents aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);



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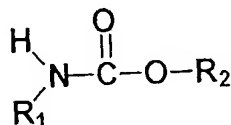
- where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and acetamide;

20



- where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20);

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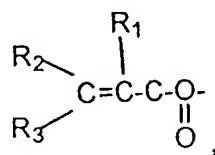


- where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and amino-substituted aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

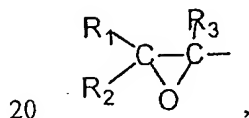
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(B) from 10 to 90 weight percent of a multifunctional cross-linking agent, said cross-linking agent consists of a backbone with at least 2 functional groups, said backbone is selected from the group consisting of:

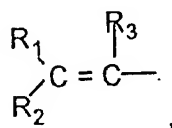
- (1) linear or branched aliphatic chains, $-(CRH)_n-$, $n=1-1000$, where R represents an aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);
 - (2) ethylene glycol chains, $-(CH_2CH_2O)_n-$ where $n=1-1000$;
 - (3) propylene glycol chains, $-(CH(CH_3)CH_2O)_n-$ where $n=1-1000$;
 - (4) cyclohexyl; and
 - (5) isocyanurate, $C_3N_3O_3$; and
- wherein the functional groups are selected from the group consisting of:
- (a) acrylates,



- where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);
- (b) carboxylic acid, $-COOH$;
 - (c) epoxides,



- where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and
- (d) vinyls,



where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

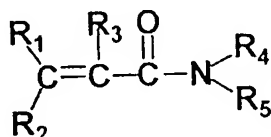
- (C) from 0.1 to 80 weight percent of an inorganic radiation sensitizer having a particle size in the range of 1 nanometer to 1000 nanometers, said radiation sensitizer is selected from the group consisting of VB-VIB semiconductors, VB-VIIB semiconductors, IIB-VIB semiconductors, IIB-VB

semiconductors, IIIB-VB semiconductors, IIIB-VIB semiconductors, IB-VIB semiconductors, and IVB-VIIB semiconductors; and

(D) 5 to 90 weight percent of a polymer.

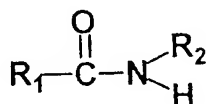
5 Additionally, this invention discloses a composition, that can be polymerized/cross-linked imagewise by ionization radiation, consisting essentially of:

(A) from 10 to 90 weight percent of a reactive monomer having at least one amide functional group, said monomer selected from the group consisting of:

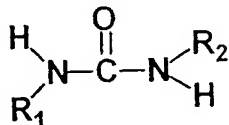


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where R_1 , R_2 , R_3 , R_4 and R_5 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, and
15 aliphatic groups with $R'O-$ substituent where R' represents aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

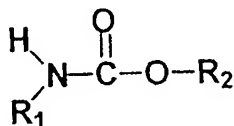


20 where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and acetamide;



25

where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20);



30

where R_1 and R_2 are selected from the group consisting of: hydrogen; aliphatic

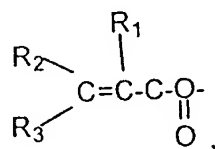
groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and amino-substituted aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

- (B) from 10 to 90 weight percent of a multifunctional cross-linking agent, said cross-linking agent consists of a backbone with at least 2 functional groups, said backbone is selected from the group consisting of:

- (1) linear or branched aliphatic chains, $-(CRH)_n-$, $n=1-1000$, where R represents an aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);
- (2) ethylene glycol chains, $-(CH_2CH_2O)_n-$ where $n=1-1000$;
- (3) propylene glycol chains, $-(CH(CH_3)CH_2O)_n-$ where $n=1-1000$;
- (4) cyclohexyl; and
- (5) isocyanurate, $C_3N_3O_3$; and

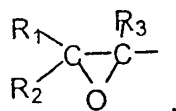
wherein the functional groups are selected from the group consisting of:

- (a) acrylates,

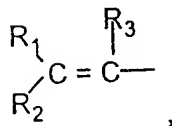


where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

- (b) carboxylic acid, $-COOH$;
- (c) epoxides,



- where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and
- (d) vinyls,



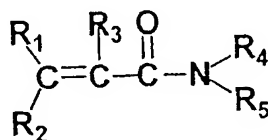
where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

- (C) from 0.1 to 80 weight percent of an inorganic radiation sensitizer

- having a particle size in the range of 1 nanometer to 1000 nanometers, said radiation sensitizer is selected from the group consisting of VB-VIB semiconductors, VB-VIIB semiconductors, IIB-VIB semiconductors, IIB-VB semiconductors, IIB-VB semiconductors, IIB-VIB semiconductors, IB-VIB semiconductors, and IVB-VIIB semiconductors;
- (D) 5 to 90 weight percent of a polymer binder; and
- (E) 5 to 90 weight percent of metallic particle or ceramic oxide fillers, said metallic filler is selected from group consisting of Al, Ti, V, Cu, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, In, and Sb; said oxide filler is selected from the group consisting of Al, Ti, V, Cu, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, In, Sb, Ta, W, and Si.

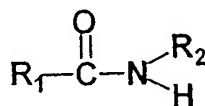
Another disclosure of this invention is a composition that can be polymerized/cross-linked imagewise by ionization radiation consisting essentially of:

- (A) from 10 to 90 weight percent of a reactive monomer having at least one amide functional group, said monomer selected from the group consisting of:



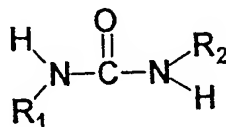
- where R_1 , R_2 , R_3 , R_4 , and R_5 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, and aliphatic groups with $R'O-$ substituent where R' represents aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

25



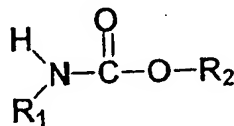
- where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and acetamide;

30



where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic

groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20);



5

where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and amino-substituted aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

10

(B) from 10 to 90 weight percent of a multifunctional cross-linking agent, said cross-linking agent consists of a backbone with at least 2 functional groups, said backbone is selected from the group consisting of:

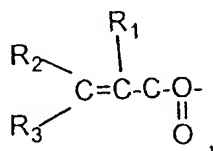
15

- (1) linear or branched aliphatic chains, $-(CRH)_n-$, $n=1-1000$, where R represents an aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);
- (2) ethylene glycol chains, $-(CH_2CH_2O)_n-$ where $n=1-1000$;
- (3) propylene glycol chains, $-(CH(CH_3)CH_2O)_n-$ where $n=1-1000$;
- (4) cyclohexyl; and
- (5) isocyanurate, $C_3N_3O_3$; and

wherein the functional groups are selected from the group consisting of:

20

(a) acrylates,

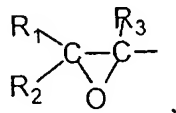


25

where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

(b) carboxylic acid, $-\text{COOH}$;

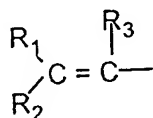
(c) epoxides,



30

where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and

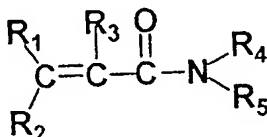
(d) vinyls,



- where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1}
 5 and C_nH_{2n-1} ($n=1$ to 20); and
 (C) 5 to 90 weight percent of a polymer binder.

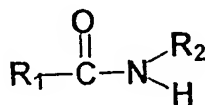
A further disclosure of this invention is a composition, that can be
 polymerized/cross-linked imagewise by ionization radiation, consisting essentially
 of:

- 10 (A) from 10 to 90 weight percent of a reactive monomer having at least
 one amide functional group, said monomer selected from the group consisting of:

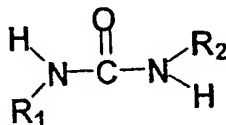


- 15 where R_1 , R_2 , R_3 , R_4 , and R_5 are selected from the group consisting of hydrogen;
 aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups
 C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, and
 aliphatic groups with $R'O-$ substituent where R' represents aliphatic group,
 C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

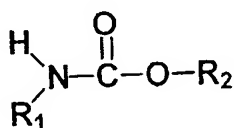
20



- where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic
 groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1}
 25 ($n=1$ to 20); and acetamide;



- 30 where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic
 groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and unsaturated aliphatic groups
 C_nH_{2n-1} ($n=1$ to 20);

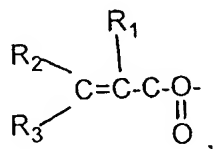


where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and amino-substituted aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

(B) from 10 to 90 weight percent of a multifunctional cross-linking agent, said cross-linking agent consists of a backbone with at least 2 functional groups, said backbone is selected from the group consisting of:

- 10 (1) linear or branched aliphatic chains, $-(CRH)_n-$, $n=1-1000$, where R represents an aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);
- (2) ethylene glycol chains, $-(CH_2CH_2O)_n-$ where $n=1-1000$;
- (3) propylene glycol chains, $-(CH(CH_3)CH_2O)_n-$ where $n=1-1000$;
- (4) cyclohexyl; and
- 15 (5) isocyanurate, $C_3N_3O_3$; and wherein the functional groups are selected from the group consisting of:

(a) acrylates,



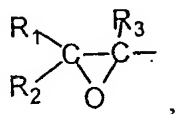
20

where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

(b) carboxylic acid, $-\text{COOH}$;

(c) epoxides,

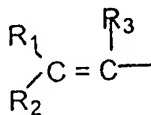
25



where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and

30

(d) vinyls,



where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

5 (C) 5 to 90 weight percent of a polymer binder; and

(D) 5 to 90 weight percent of metallic or oxide fillers, said metallic filler is selected from group consisting of Al, Ti, V, Cu, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, In, and Sb; said oxide filler is selected from the group consisting of Al, Ti, V, Cu, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, In, Sb, Ta, W, and Si.

10 This invention also discloses methods to use these compositions for microfabrication of ceramics, for stereolithography and as photoresists in x-ray, e-beam, and ion-beam lithography. Disclosed in this invention is a method of microfabricating ceramic or metal patterns on a solid substrate using ionization radiation comprising the steps of:

15 (i) mixing together a composition consisting essentially of a reactive monomer, a multi-functional cross-linking agent and filler; said mixing process optionally carried out either by heating the composition until melted or by dissolving components in a common solvent;

optionally, in the presence of binder; and

20 optionally, in the presence of a radiation sensitizer;

(ii) casting the composition on a solid substrate to form a film of desired thickness;

(iii) irradiating the film with ionization radiation through a mask to form a polymerized/cross-linked image;

25 (iv) developing the polymerized/cross-linked image by rinsing the irradiated film in a solvent to remove unirradiated composition; and
(v) sintering the polymerized/cross-linked image in microfabricated ceramics or metal patterns.

30 This invention also discloses a method of performing lithography on a semiconductor surface using ionization radiation, comprising the steps of:

(i) mixing a composition consisting essentially of a reactive monomer and a multi-functional cross-linking agent together, optionally by

(a) heating the composition until melted; or

(b) by dissolving in a common solvent;

35 optionally, in the presence of a polymer binder; and
optionally, in the presence of a radiation sensitizer;

(ii) casting the composition on a solid substrate to form a film of desired thickness;

(iii) irradiating the film with ionizing radiation through a mask to form a polymerized/cross-linked image; and

5 (iv) developing the polymerized/cross-linked image by rinsing the irradiated film in a solvent to remove unirradiated composition.

A further method disclosed in this invention is a method of forming a three-dimensional solid object of polymers, ceramics, or metals using ionization radiation, comprising the steps of:

10 (i) mixing together a composition consisting essentially of a reactive monomer, a multi-functional cross-linking agent, and a polymer binder, said mixing process optionally done by dissolving in a common solvent or by pouring the composition into a container with a target substrate immersed in it;

optionally, in the presence of a radiation sensitizer; and
15 optionally, in the presence of a metallic or oxide filler;

(ii) irradiating the composition with ionization radiation through a mask or a focused source of ionization radiation to deposit a layer of material on the targeted substrate;

(iii) stepping back the substrate and irradiating the substrate;

20 (iv) repeating the step of stepping back the substrate and irradiating the substrate until a desired three-dimensional solid object is formed; and optionally, treating the solid object post-irradiation.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic illustration of a method of microfabrication of
25 ceramics using ionization radiation imageable photopolymer compositions.

Figure 2 is a schematic illustration of the method of stereolithography using x-ray imageable photopolymer compositions to fabricate three-dimensional ceramics or metal objects.

Figure 3 is a schematic illustration of the method of x-ray lithography
30 using x-ray imageable photopolymer compositions.

Figure 4 is an optical micrograph of an image developed in accordance with Example 61 of the present application. The dark region represents the polymerized/cross-linked region, the width of which is about 140 microns.

DETAILED DESCRIPTION OF THE DRAWINGS

35 Figure 1 is a schematic illustration of a method of microfabrication of ceramics using ionization radiation imageable photopolymer compositions disclosed in this invention. The reference numbers provided here correspond to the reference numbers of Figure 1. Figure 1A shows ionization radiation

imageable photopolymer composition, 1; and a substrate, 2. Arrow 3 represents exposure of the composition to ionization radiation imagingwise. Figure 1B shows a mask, 5; unexposed region of imageable photopolymer composition (or unirradiated composition), 1; and cross-linked polymer/ceramics, 7, resulting from the ionization radiation exposure of the imageable photopolymer composition. Figure 1C shows a representation of the removal of solvent to accomplish washing away the region of the substrate unexposed to the ionization radiation, 6, and cross-linked polymer/ceramics, 7. Arrow 8 represents the sintering step to burn out polymer binders. Figure 1D shows the micofabricated ceramics, 9, and the substrate, 2.

Figure 2 is a schematic illustration of a method of stereolithography using x-ray imageable photopolymer compositions to fabricate three-dimensional ceramics or metal objects. The reference numbers here correspond to the reference numbers of Figure 2. Figure 2A shows a representation of a substrate, 10, a x-ray imageable polymer/ceramics or polymer/metal compositions disclosed in this invention, 11, and a container, 12. Arrow 13 represents a first exposure of the composition to ionization radiation imagingwise. Figure 2B shows a representation of cross-linked polymer/ceramic or polymer/metal, 14, after the first exposure to a scanning beam of ionization radiation, 15, such as x-ray or e-beam. Arrow 16 represents stepping back the substrate to allow for a second exposure of the composition to ionization radiation imagingwise. Figure 2C represents cross-linked polymer/ceramic or polymer/metal, 17, after the second exposure to a scanning beam of ionization radiation, 15, such as x-ray or e-beam. Arrow 18 represents stepping back the substrate, 10, to allow for a third exposure of the composition to ionization radiation imagingwise. Figure 2D is a representation of cross-linked polymer/ceramic or polymer/metal, 19, after the third exposure of the composition to ionization radiation imagingwise. Arrow 20 represents repetition of the stepping back and exposure steps until a desired shape/thickness is reached. Figure 21E is a representation of an object formed by a method of this invention comprising cross-linked polymer/ceramic or polymer/metal. Arrow 22 represents an optional sintering step to burn out polymer binders. Figure 23F is a representation of an object made of ceramics or metal in accordance with the method of this invention.

Figure 3 is a schematic illustration of the method of x-ray lithography using x-ray imageable photopolymer compositions. E-beam can be used to replace x-ray. The numbers provided here correspond and refer to numbers shown in Figure 3. Figure 3A shows a representation of a x-ray imageable photopolymer composition, 100, disclosed in this invention and a substrate, 101, such as silicon

wafer. Arrow 102 represents exposure of substrate to x-ray imagingwise. Figure 3B shows x-ray beams, 103, and a x-ray mask, 104, unexposed regions of the x-ray imageable photopolymer composition, 100, and cross-linked polymers, 106. Arrow 105 represents the step of removing unexposed regions of the composition by washing with solvent. Figure 3C represents cross-linked polymers, 106, and conventional wafer processing procedures, 107, such as etching or doping.

Figure 4 is an optical micrograph of an image developed in accordance with Example 61 of the present invention. The dark regions are the polymerized/cross-linked regions which has of width of about 140 microns.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of this invention comprise five parts: (1) reactive monomer, (2) multi-functional cross-linking agent, (3) radiation sensitizer, (4) polymer binder, and (5) filler. The required components are the reactive monomer and the multi-functional cross-linking agent. Both have to be combined synergistically to form an effective composition. The absence of either one is not acceptable. The radiation sensitizer, polymer binder, and filler are required under some conditions and for certain applications. The effective composition has to show sufficient solubility change in a selected solvent after being irradiated by ionizing radiation such as x-ray, high-energy electron beam or gamma ray. This solubility change has to be confined only in the area that receives ionization radiation (that is, with good spatial resolution). For practical purposes, sufficient solubility change must be achieved with relatively low intensity radiation, such as those produced by a laboratory x-ray machine, rather than synchrotron radiation, which is more expensive. It should be achieved within a reasonably short duration preferably within about 1 hr or shorter.

To have a useful x-ray imageable photopolymer composition, many properties are required. The composition has to be able to polymerize/crosslink under relatively low intensity of x-ray beams such as those commonly used for x-ray diffraction, medical diagnostics and inspection. Some monomers/polymers (e.g., PMMA) can be polymerized/cross linked by high intensity synchrotron radiation but not under the irradiation of lower intensity laboratory x-ray machines. The exposure time required for polymerization/cross-linking should be as short as possible, preferably within an hour or less. The polymerized/cross-linked region should show large differentiation in solubility in certain solvents so the image can be developed by simply dissolving away the unexposed region. In order to retain the required spatial resolution, this differentiation in solubility between exposed and unexposed region has to be

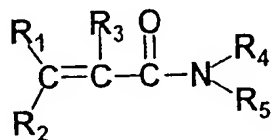
significant. In addition, the polymerization/cross-linking reaction has to be confined in the imaged area to maintain good spatial resolution.

The compositions should have thermal stability and long shelf life and preferably should be light stable to allow easy handling. For applications requiring the use of thin films, the composition should have the right properties, such as optimal viscosity, for the casting of good quality thin film. For applications involving the additions of fillers such as ceramics and metal particles, the composition has to be optimized to maintain the structural integrity after image development and sintering at high temperature.

One objective of this invention is to develop materials that can be polymerized/cross-linked imagewise by relatively low intensity ionization radiation, such as x-ray, e-beam or gamma ray, within a short duration. A further objective is to develop materials and technologies that are useful for micro-fabrication of ceramics, stereolithography, and x-ray (e-beam) lithography.

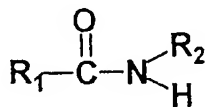
(A) monomers:

Effective monomers have the following general structures:



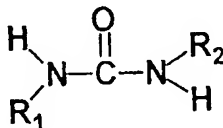
where R_1 , R_2 , R_3 , R_4 , and R_5 are selected from: hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, or aliphatic groups with $R'O-$ substituent where R' represent aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20).

Additional effective monomers have the general structures:



where R_1 and R_2 are selected from: hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); or acetamide.

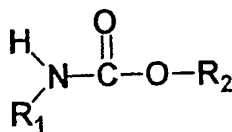
Additional effective monomers have the general structures:



where R_1 and R_2 are selected from: hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); or unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20).

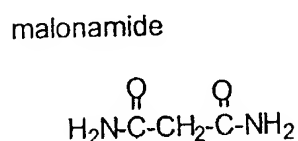
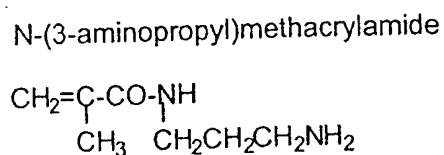
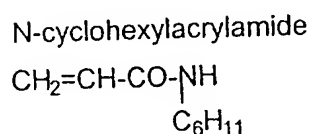
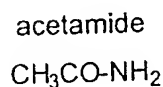
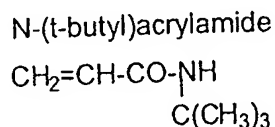
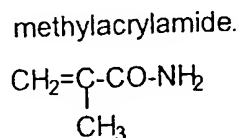
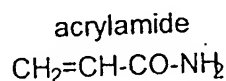
Additional effective monomers have the general structures:

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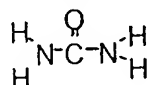


where R_1 and R_2 are selected from: hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); or
 10 amino-substituted aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20).

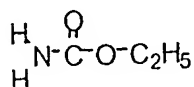
The most preferred monomers are:



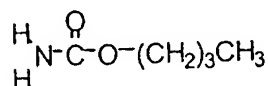
urea



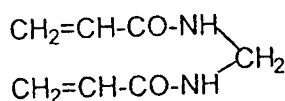
urethane



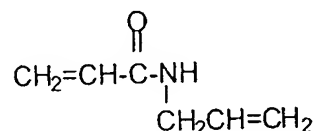
butylcarbamate



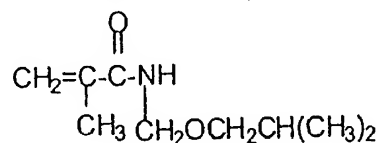
N,N'-methylenebisacrylamide



N-allylacrylamide

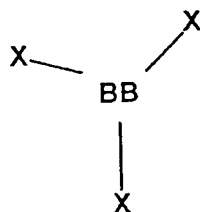


N-(iso-butoxymethyl)methylacrylamid

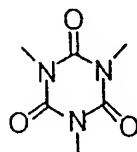


5 (B) Multi-functional cross-linking agents:

The effective cross-linking agents consist of a backbone (BB) connected with at least 2, preferably 2 to 4, most preferably 2 to 3 functional groups. This is shown schematically below:

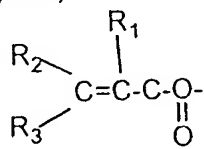


- The choice of backbone affects the mechanical properties, the solubility properties, and the film coating properties of the composition. The preferred backbones are (1) linear or branched aliphatic chains, $-(CRH)_n-$, $n=1-1000$, where R represents an aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); (2) ethylene glycol chains, $-(CH_2CH_2O)_n-$ where $n=1-1000$; (3) propylene glycol chains, $-(CH(CH_3)CH_2O)_n-$ where $n=1-1000$; (4) saturated cyclic hydrocarbons such as cyclohexyl; and (5) isocyanurate, $C_3N_3O_3$, shown below.



- The choice of the functional group, X, determines the reactivity of the composition and the extent of polymerization/cross-linking in the irradiated product. The reactivity cannot be too high such that thermal polymerization occurs in the absence of x-ray. In general more than one functional group is needed for effective cross-linking and fast polymerization. A cross-linking agent may contain the same functional groups or different combinations of effective functional groups. Preferred functional groups are:

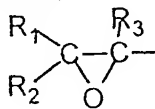
- (1) acrylates,



, where R_1 , R_2 , and R_3 are selected from hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

- (2) carboxylic acid, $-COOH$;

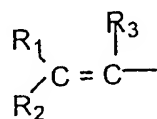
- (3) epoxides,



, where R_1 , R_2 , and R_3 are selected from: hydrogen or

aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

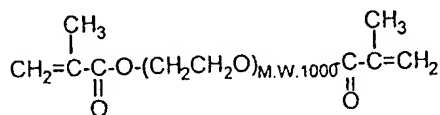
- and (4) vinyls,



, where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20).

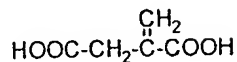
The most preferred cross-linking agents are:

PEG(1000)dimethylacrylate

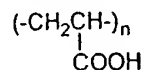


malonic acid
 $HOOC-CH_2-COOH$

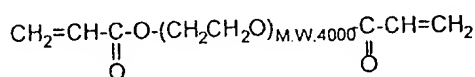
itaconic acid



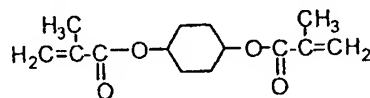
polyacrylic acid



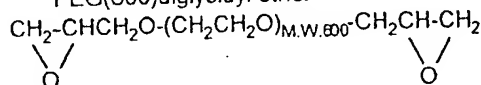
PEG(4000)diacrylate



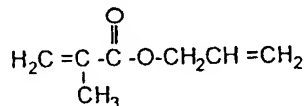
1,4-cyclohexanediol dimethacrylate



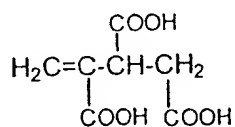
PEG(600)diglycidyl ether



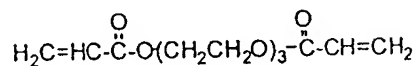
allyl methacrylate



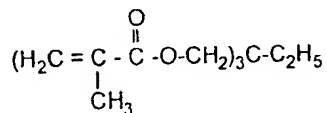
3-butene-1,2,3-tricarboxylic acid



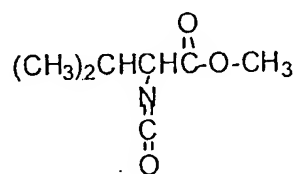
triethylene glycol diacrylate



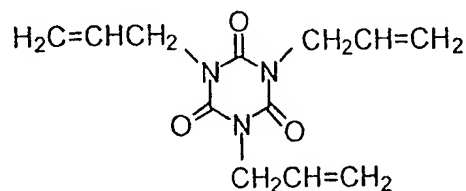
1,1,1-trimethylolpropane trimethacrylate



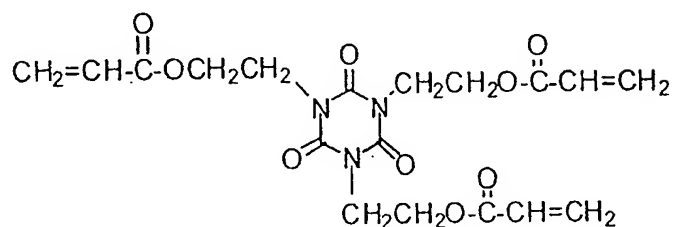
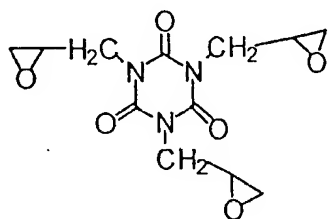
methyl-2-isocyanato-3-methylbutyrate



triallylisocyanurate



tris(2-acryloxyethyl)isocyanurate

tris(2,3-epoxypropyl)isocyanurate
(triglycidyl isocyanurate)

(C) Radiation sensitizers

- 5 The number of reactive species generated per unit volume for initiating polymerization reaction is low due to the low absorption cross-section of x-ray, e-beam, and gamma ray in organic media. The x-ray absorption efficiency of the composition may be improved by the addition of inorganics. If the particle size of the inorganics is too large, for example, in the microns size regime, the initially

generated electrons and holes would recombine within the inorganic particle and disappear. Therefore, the inorganic particles have to be small enough, preferably in the nanometer-size regime, so that electrons and holes can escape to the surrounding media and initiate chemical reactions. The preparation of nanometer sized inorganic particles have been disclosed by U.S. 5,556,716 (September 17, 1996, Herron and Wang); U.S. 5,132,051 (July 21, 1992, Herron and Wang); U.S. 5,238,607 (August 24, 1993, Herron and Wang), which are incorporated herein by reference; Res. Chem. Interm., 15, 17-29(1991), Y. Wang and N. Herron; J. Phys. Chem., 95, 525 (1991), Y. Wang and N. Herron.

The addition of inorganic radiation sensitizer enhances the x-ray absorption efficiency of the composition. It can also affect the polymerization/cross-linking kinetics, the overall reaction rate, and the cross-linking density of the irradiated region. Preferably, the inorganics should contain strong radiation-absorbing heavy atoms such as Bi, Pb, Hg, Au, Pt, and I and should be able to disperse easily into the composition, preferably in 0.1-80 wt. % range. Preferable, their size should be in the range of 1 nm to 1000 nm. The most preferred size range is 1 nm to 100 nm.

The inorganic nanoparticles are selected from the group consisting of VB-VIB semiconductors, VB-VIIB semiconductors, IIB-VIB semiconductors, IIB-VB semiconductors, IIIB-VB semiconductors, IIIB-VIB semiconductors, IB-VIB semiconductors, and IVB-VIIB semiconductors. The preferred inorganic nanoparticles are selected from the group consisting of Bi_2S_3 , Bi_2Se_3 , BiI_3 , BiBr_3 , HgS , PbI_2 , PbI_4^{-2} , and $\text{Pb}_2\text{I}_7^{-3}$. The most preferred inorganic nanoparticle is BiI_3 .

(D) Binders:

The binder is defined here as a high molecular weight (>1000) polymer. The use of binders in the formulation serves many purposes. Certain monomers, such as acrylamide, have a tendency to crystallize, which not only reduces the x-ray sensitivity of the composition but also affects the spatial resolution of the x-ray imaged area. The addition of binders can prevent such monomer crystallization problem. Certain compositions of monomer and cross-linking agent, such as acrylamide and malonic acid, though polymerizable by x-ray irradiation, show uncontrolled polymerization and cannot retain the x-ray image. The addition of suitable binders can confine the polymerization in the irradiated region, thereby forming a useful x-ray image. The addition of binder can also enhance the film casting and handling properties which improves the ease of film preparation. Binders can also control the mechanical and chemical properties of the polymerized/cross-linked product.

The selection of binder depends on the composition of the monomer and the cross-linking agent used as well as the targeted application. The binder should be miscible with the monomer, the cross-linking agents, and, if used, the radiation sensitizer. For applications involving microfabrication of ceramics such as barrier
5 rib fabrication for plasma display, the binder used should be burned out easily during the sintering step. Acrylate based polymer and polyethylene binders can be used for this purpose. When the application is stereolithography, the mechanical strength and dimensional stability of the polymerized material are important. Acrylate and epoxy-based polymers as well as polyamides are effective binders for
10 this application. When the application is lithography, the binder selected has to be stable under a plasma environment during the etching step in semiconductor manufacturing. Epoxy based polymers and polyamides are effective for this application. When aqueous based compositions are used, for example when environmental concerns are important, water-soluble polymers such as
15 polyacrylamide, polyvinylalcohol, and polyethyleneglycol are suitable.

The preferred binders are acrylate polymers, acrylate-acrylic acid polymers such as CARBOSET xpd2470, available commercially from BF Goodrich Specialty Chemicals, Cleveland, Ohio, and related polymers), epoxy polymers, polyamides, polyacrylamides, polyvinylalcohol, poly(ethylene)glycol,
20 poly(propylene)glycol, polyethylene, and polyvinylacetate.

(E) Fillers:

The compositions disclosed above can be mixed with ceramic particles or metal particles to form radiation sensitive composites. Using radiation (x-ray, electron beam, or gamma ray) imaging techniques, these compositions can then be
25 fabricated into ceramic or metal objects after burning out the organics. The fillers used should not absorb radiation too strongly or they will reduce sensitivity. The surfaces of the fillers should not be reactive toward the monomers and cross-linking agents used in the compositions to avoid thermal polymerization. Suitable metal particle fillers consist of Al, Ti, V, Cu, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, In, and Sb. The preferred metal particle fillers are Al, Cu, Fe, Co, Ni,
30 and Cu. The most preferred filler is Al. Suitable ceramic particle fillers consist of the oxides of Al, Ti, V, Cu, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, In, Sb, Ta, W, and Si. The preferred ceramic particle fillers are oxides of Al, Ti, Fe, Ni, Zn, Ta, W, and Si. The most preferred are aluminum oxides and silicon oxides.

35 (F) Preparation of radiation-imageable photopolymer compositions:

The x-ray imageable compositions can be prepared by either the melt route or the solution route. Certain monomers, cross-linking agents, and radiation sensitizers, such as acrylamide, poly(ethyleneglycol)_n dimethacrylate, and BiI₃,

can be melted together. Solid thin film can then be formed by casting or extrusion from the melt. A more flexible method is to use a common solvent to dissolve all components together. For example, dimethylformamide is effective to dissolve acrylamide, poly(ethyleneglycol)_n, dimethacrylate, BiI₃, and CARBOSET xpd2470
5 binder together. This solution can be used directly for applications such as stereolithography; or solid films can be prepared from the solution by spin-coating or screen printing techniques.

(G) Radiation sources:

The radiation source used in this invention is defined as ionization
10 radiation, typically consisting of gamma ray, x-ray, electron beam, and ion beam. Gamma ray can be produced conveniently from radioactive isotopes such as ⁶⁰Co. X-ray beam can be generated by electron bombardment of metal target or from synchrotron machine. Commonly used targets are W, Mo, and Cu. Electron beam can be generated by electron accelerator. Since the applications disclosed in this
15 invention require radiation-induced polymerization to proceed with well-defined spatial resolution, a mask is usually required. When selecting the radiation source, the selection of mask material is an important consideration. The thickness of the mask material has to increase to compensate for the lower absorption efficiency with higher energy ionization radiation such as gamma ray.
20 The preferred radiation sources are x-ray and electron beam. The most preferred source is x-ray.

(1) Microfabrication of ceramics: Microfabrication of ceramics are required for applications such as piezoelectrics and plasma display. Traditional microfabrication technique such as photolithography is not applicable because of
25 the opaque nature of ceramic paste. The use of x-ray sensitive polymer/ceramic compositions can solve this problem. This is elaborated in the following for the fabrication of barrier ribs in plasma flat panel display.

In a typical plasma display device, special gas mixtures containing Xe or Ar are encapsulated in a cell, representing a pixel in a display device, with walls
30 made of ceramics such as silica and alumina. The cell walls are coated with display phosphors with electrodes located at both ends. The application of a sufficiently large voltage across the electrodes breaks down the gases, which emit UV light, and excites the phosphors to produce the desired blue, green or red luminescence. The fabrication of the ceramic cell walls (or barrier ribs), with a
35 typical dimension of 50-75 microns in width and 150-200 microns in height, is a challenge. The current preferred method involves repeated exposure of a very thin photopolymer/ceramic mixture film with photolithography to build up the thickness, layer by layer. This method is not acceptable for mass production

because it is very slow and expensive. Use of the x-ray sensitive photopolymer/ceramic compositions disclosed in this invention allows a thicker layer to be formed with one-x-ray exposure. The basic principle is illustrated schematically in Figure 1 below. The invention may be practiced in many different ways and is not limited to the configuration described here.

The feasibility of this application is exemplified in the Examples using x-ray sensitive compositions mixed with alumina and silica. The mixtures were polymerized/cross-linked imagewise by x-ray. The unexposed regions were easily washed out with solvents to reveal cross-linked solid images consisting of polymer/ceramic composite. This technology, as illustrated in Figure 1, can be used to fabricate barrier ribs for plasma flat panel display.

(2) Stereolithography: There is a growing need for the rapid prototyping of three-dimensional (3D) objects from a computer aided design program. Such solid objects are needed for visualization, design modification, function checking, etc. Current technology consists of exposing a photopolymer composition using a scanning laser to form a cross-linked solid layer and then building up to a solid object layer by layer by stepping back the substrate as shown in Figure 2. The photopolymer film has to be fairly thin with a typical thickness of 100-150 microns and the dimension of the finished object can be up to 1/2 meter. There is a market need for fabricating ceramic and metal objects which is difficult for the optical based photopolymer technology to deliver. The ionization radiation imageable photopolymer/ceramic and photopolymer/metal compositions disclosed of the present invention can address this problem. The basic principle is illustrated schematically in Figure 2 below. The invention may be practiced in many different ways and is not limited to the configuration described here.

The feasibility of this application was demonstrated in the Examples given in this invention using x-ray sensitive compositions mixed with alumina, silica, or aluminum metal powders. The mixture was polymerized/cross-linked imagewise by x-ray. The unexposed region was easily washed out with solvents to reveal a cross-linked solid image consisting of polymer/ceramic composite or polymer/metal composite.

(3) X-ray lithography: X-ray lithography is being developed for the fabrication of a future generation of semiconductor devices with feature size as small as 30 nm (0.03 microns). Currently, there is no ideal photoresist for x-ray lithography. For example, PMMA thin film is used for this purpose but high intensity synchrotron radiation has to be used for writing an image (by ablation of the film). This is suitable for research purpose, but is not practical. The x-ray sensitive compositions disclosed in this invention can be used for this purpose.

The working of a negative photoresist is illustrated schematically in Figure 3. The invention may be practiced in many different ways and is not limited to the configuration described here.

Experimental apparatus

5 The X-ray exposure experiments were performed using a Siemens x-ray generator equipped with a broad focus Mo-tube operating at 40 KV and 40 milliamp current. The incident x-ray dose rate was measured to be 6.1×10^4 roentgen/minute. By definition, the exposure of air to 1 roentgen(R) liberates a total electrical charge of 2.58×10^{-4} coulombs per kilogram of air. When 1 cm³ of
10 air is given 1 roentgen of x-ray, the absorbed dose is 0.87 rad ("Radiation Chemistry", A. J. Swallow, Wiley, New York, 1973).

COMPARATIVE EXAMPLE A

3.496 g of acrylamide was melted at ~85°C. Films were casted with the melt on glass substrates. The films were irradiated by a x-ray beam from a Mo
15 target for 10 and 30 minutes. The films were then developed by washing with water. The irradiated region showed a decrease in solubility but no insoluble image can be developed. This example demonstrates that compositions containing only reactive monomer such as acrylamide are not effective.

COMPARATIVE EXAMPLE B

20 A total of 4.543 g of acrylamide was added to 2.0 g of distilled water slowly over a period of 40 minutes and was stirred at room temperature overnight. The clear homogeneous solution was then diluted with 3.603 g of distilled water, making the concentration of acrylamide was 39.6%. Filled a glass vial (1.5 cm diameter) with some of the solution. The vial was irradiated by a x-ray beam from
25 a Mo target for 30 minutes. The formation of an irregular shaped gel can be observed but no well-defined insoluble image can be obtained. This example demonstrates that although in aqueous solution the polymerization of acrylamide is enhanced compared to that in the solid state, the polymerization reaction cannot be controlled spatially and the polymerization product is not sufficiently insoluble,
30 therefore is not useful for the applications considered in this invention.

COMPARATIVE EXAMPLE C

3.881 g of polyacrylamide/water solution (50/50) was irradiated in a glass vial by a x-ray beam from a Mo target for 30 minutes. There was no change in the solution after irradiation. This example demonstrates polyacrylamide alone is not
35 effective.

EXAMPLE 1

2.503 g of acrylamide and 0.498 g of poly(ethyleneglycol)_ndimethacrylate (PEGDMA), n=1000 in molecular weight, were mixed together and melted at

- ~85°C. 1.148 g of BiI_3 was added to the melt while stirring. The melt was casted onto a glass substrate to form a film. The film had orange-red color, rather than the black color characteristic of bulk BiI_3 . This indicates the existence of nano- BiI_3 . The film was irradiated by a x-ray beam from a Mo target for 1 hour.
- 5 The film was then developed by washing with water. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 2

- 1.449 g of acrylamide and 1.001 g of PEGDMA were mixed together and melted at ~85°C. 1.001 g of BiI_3 was added to the melt while stirring. The melt
- 10 was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for 1 hour. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 3

- 1.498 g of acrylamide and 0.996 g of PEGDMA were mixed together and
- 15 melted at ~85°C. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for 1 hour. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated. Initially the spot was well defined spatially, but the spot
- 20 swore when water was left on it for a few hours. This swelling was absent for compositions containing nano- BiI_3 . This result indicates that after x-ray irradiation the cross-linking density is higher with compositions containing nano- BiI_3 .

EXAMPLE 4

- 2.254 g of acrylamide and 1.54 g of PEGDMA were mixed together and
- 25 melted at ~85°C. 0.417 g of BiI_3 was added to the melt while stirring. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for 15 minutes. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 5

- 3.009 g of acrylamide and 2.005 g of PEGDMA were mixed together and melted at ~85°C. 2.003 g of BiI_3 was added to the melt while stirring. 10.503 g of alumina was added to the mixture. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for
- 35 1 hour. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 6

0.761 g of acrylamide and 0.507 g of poly(ethyleneglycol)_{M.W.~4000} diacrylate were mixed together and melted at ~85°C. The melt was casted onto two separate glass substrates to form solid films. The films were irradiated by a x-ray beam from a Mo target for 15 minutes and 30 minutes, respectively. The films were then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 7

1.54 g of acrylamide and 1.011 g of poly(ethyleneglycol)_{M.W.~600} diglycidyl ether were mixed together and melted at ~85°C. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for 10 minutes. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 8

2.998 g of acrylamide and 2.01 g of PEGDMA were mixed together and melted at ~85°C. 0.59 g of polyacrylamide (5-6 million molecular weight) was added to the melt while stirring. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for 30 minutes. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 9

2.515 g of acrylamide and 2.018 g of PEGDMA were mixed together and melted at ~85°C. 0.505 g of N-(3-aminopropyl)methacrylamide was added to the melt while stirring. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for 10 minutes. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 10

3.006 g of acrylamide and 2.009 g of PEGDMA were mixed together and melted at ~85°C. 3.013 g of alumina particles was added to the melt while stirring. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for 1 hr. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 11

3.011 g of N-(iso-butoxymethyl)methylacrylamide and 1.996 g of PEGDMA were mixed together and melted at ~85°C. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo

target for 1 hr. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 12

2.996 g of acrylamide and 2.011 g of PEGDMA were mixed together and
5 melted at $\sim 85^{\circ}\text{C}$. 2.043 g of BiI_3 was added to the melt while stirring. 4.684 g of aluminum metal particles (20 microns) was then added to the mixture. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for 30 min. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam
10 irradiated.

EXAMPLE 13

3.001 g of acrylamide and 1.997 g of PEGDMA were mixed together and
melted at $\sim 85^{\circ}\text{C}$. 3.336 g of aluminum metal particles (20 microns) was then
added to the mixture. The melt was casted onto a glass substrate to form a film.
15 The film was irradiated by a x-ray beam from a Mo target for 10 min. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 14

3.0 g of methylacrylamide and 1.997 g of PEGDMA were mixed together
20 and melted at $\sim 110^{\circ}\text{C}$. The melt was poured into a 1.5 cm vial. The vial was irradiated by a x-ray beam from a Mo target for 10 min. The contents of the vial were then developed by washing with water. An insoluble plug was formed only at where the x-ray beam irradiated.

EXAMPLE 15

3.505 g of acetamide and 2.328 g of PEGDMA were mixed together and
25 melted at $\sim 85^{\circ}\text{C}$. The melt was poured into a 1.5 cm vial. The vial was irradiated by a x-ray beam from a Mo target for 30 min. The content of the vial was then developed by washing with water. An insoluble plug was formed at where the x-ray beam irradiated.

30

EXAMPLE 16

3.507 g of n-cyclohexylacrylamide and 2.336 g of PEGDMA were mixed
together and melted at $\sim 120^{\circ}\text{C}$. The melt was casted onto a glass substrate to
form a film. The film was irradiated by a x-ray beam from a Mo target for 10 min.
The film was then developed by washing with water. An insoluble spot was
35 formed at where the x-ray beam irradiated.

EXAMPLE 17

3.008 g of acrylamide and 2.0 g of 3-butene-1,2,3-tricarboxylic acid were
mixed together and melted at $\sim 135^{\circ}\text{C}$. The melt was poured into a 1.5 cm vial.

The vial was irradiated by a x-ray beam from a Mo target for 10 min. The content of the vial was then developed by washing with water. An insoluble plug was formed at where the x-ray beam irradiated.

EXAMPLE 18

5 3.003 g of acrylamide and 2.009 g of PEGDMA were mixed together and melted at ~85°C. 0.063 g of polyethylene was then added to the mixture. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for 10 min. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam
10 irradiated.

EXAMPLE 19

 3.01 g of acrylamide and 2.014 g of PEGDMA were mixed together and melted at ~85°C. 0.267 g of malonic acid was then added to the mixture. The melt was casted onto a glass substrate to form a film. The film was irradiated by a
15 x-ray beam from a Mo target for 2.5 min. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 20

 3.004 g of acrylamide and 2.006 g of PEGDMA were mixed together and
20 melted at ~85°C. 0.477 g of poly(propyleneoxide)cyclocarbonate terminated was then added to the mixture. The melt was casted onto a glass substrate to form a film. The film was irradiated by a x-ray beam from a Mo target for 10 min. The film was then developed by washing with water. An insoluble spot was formed at where the x-ray beam irradiated.

EXAMPLE 21

25 3.003 g of n-cyclohexylacrylamide and 2.002 g of PEGDMA were mixed together and melted at ~118°C. The melt was casted onto two separate glass substrates to form films. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. The substrates were developed by washing with
30 water. An insoluble spot was formed where the x-ray beam irradiated in both cases.

EXAMPLE 22

 A mixture was prepared consisting of 3.008 g of acrylamide, 1.998 g of PEGDMA and 5 mls of DMF. 2.998 g of Carboset XPD2470 polymer binder was
35 added to 6.711 g of the mixture prepared above and was stirred at room temperature for ~70 hours (no heat was required). Films were casted onto two separate glass substrates, and a glass vial (1.5 cm diameter) sample was prepared. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes,

respectively, both giving positive results. An insoluble spot was formed where the x-ray beam irradiated. The vial sample was irradiated for 30 minutes and a solid white plug, a replica of the x-ray beam, was formed.

EXAMPLE 23

5 Added 3.000 g of acrylamide and 2.009 g of PEGDMA to a mixture of 0.509 g of Carboset XPD2470 and 5 mls of DMF. The mixture was stirred at RT for 1 hour. Two glass vials were filled with the solution and irradiated by a x-ray beam from a Mo target for 30 and 60 minutes and a solid white plug, a replica of the x-ray beam, was formed in both cases.

10 EXAMPLE 24

0.998 g of Carboset XPD2470 and 5 mls of DMF were mixed together and stirred at RT for 1 hour. 3.008 g of acrylamide and 2.000 g of PEGDMA were then added and the mixture was stirred at RT for 3 hours. A 1.5 cm diameter glass vial was filled with some of the solution and a film was casted on a glass
15 substrate. Both were irradiated by a x-ray beam from a Mo target for 30 minutes. A solid white plug, a replica of the x-ray beam, was formed in the vial sample, while the film sample gave an insoluble spot where the x-ray beam irradiated after developed with acetone.

EXAMPLE 25

20 Example 27 was repeated as described above but with the following amounts: 5 mls DMF, 2.005 g XPD2470, 3.008 g acrylamide and 2.008 g PEGDMA. Both the vial and film samples gave positive results as described in Example 27.

EXAMPLE 26

25 Prepared a mixture of 2.500 g Carboset XPD2470, 10 mls DMF, 5.997 g acrylamide and 3.992 g PEGDMA and stirred at room temperature for ~1.5 hours. 0.330 g of BiI_3 and 2.998 g of the above mixture were mixed together and stirred at room temperature for 20 minutes. Films were casted on glass substrates and irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. Both gave
30 positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 27

Prepared a mixture of 2.500 g Carboset XPD2470, 10 mls DMF, 5.997 g acrylamide and 3.992 g PEGDMA and stirred at room temperature for ~1.5 hour.
35 1.930 g of silica glass particles (70.9% SiO_2 , 11.6% CaO , 8.7% Na_2O , 7.7% K_2O , 1.1% Sb_2O_3) and 3.011 g of the above mixture were mixed together and stirred at room temperature for 20 minutes. Films were casted on glass substrates and irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. Both gave

positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 28

Prepared a mixture of 2.500 g Carboset XPD2470, 10 mls DMF, 5.997 g acrylamide and 3.992 g PEGDMA and stirred at room temperature for ~1.5 hour. 1.938 g of silica glass particles (71% SiO₂, 26% B₂O₃, 0.5% Na₂O, 1% K₂O, 1% Al₂O₃, 0.5% LiO) and 3.011 g of the above mixture were and 3.006 g of the above mixture were mixed together and stirred at room temperature for 20 minutes. Films were casted on glass substrates and irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 29

Prepared a mixture of 2.500 g Carboset XPD2470, 10 mls DMF, 5.997 g acrylamide and 3.992 g PEGDMA and stirred at room temperature for ~1.5 hour. 0.321 g of polyvinyl alcohol and 3.008 g of the above mixture were mixed together and stirred at room temperature for 3 hours. Films were casted on glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. Both film samples gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

COMPARATIVE EXAMPLE D

5.812 g of acrylamide and 5.811 g of malonic acid was mixed together and heated at 85°C to form a viscous liquid. A glass vial (1.5 cm diameter) was filled with some of the melt. The vial was irradiated by a x-ray beam from a Mo target for 15 minutes. The entire contents of the vial was polymerized to form an opaque, gel-like polymer without well-defined spatial pattern of the x-ray beam.

EXAMPLE 30

3.01 g of acrylamide and 2.0 g of malonic acid were mixed together with a solution of 1.252 g of Carboset XPD2470 and 5 mls of DMF and heated to ~95°C. Films were cast onto two separate glass substrates, and a glass vial was filled with some of the solution. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes, respectively. The vial was irradiated for 30 minutes. Both film samples gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated. A solid white plug, a replica of the x-ray beam, was formed in the vial sample.

EXAMPLE 31

3.004 g of acrylamide, 2.009 g of PEGDMA and 5 mls of DMF were mixed together and heated to ~60°C. A total of 1.251 g of polyethylene glycol was added over ~30 minutes. Films were casted from the viscous melt on glass

substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

A stock solution of 62.501 g of Carboset XPD2470 and 250 mls of DMF was made and used in the preparation of Examples 36 to 48:

EXAMPLE 32

5.971 g of the stock Carboset XPD2470/DMF solution, 2.500 g of acrylamide and 2.518 g of trimethylolpropane triethoxy triacrylate (TMPEOTA) were mixed together and heated to ~85°C. Films were casted on glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 33

5.980 g of the stock Carboset XPD2470/DMF solution, 2.498 g of acrylamide and 2.498 g of itaconic acid were mixed together and heated at ~130°C. Films were casted onto two glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes, respectively. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 34

5.977 g of the Carboset XPD2470/DMF solution, 3.031 g of polyacrylic acid (90,000 MW) and 2.506 g of acrylamide were mixed together and heated to ~120°C. Films were casted onto two glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes, respectively. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 35

5.990 g of the Carboset XPD2470/DMF solution, 2.497 g of acrylamide and 2.503 g of 1,6-cyclohexandiol dimethylacrylate were mixed together and heated at ~75°C. Films were casted on glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 36

5.985 g of the Carboset XPD2470/DMF solution, 2.501 g of acrylamide and 2.510 g of allyl methacrylate were mixed together and heated to ~85°C. Films were casted onto two separate glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes, respectively. Both gave

positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 37

5.988 g of the Carboset XPD2470/DMF solution, 2.503 g of acrylamide and 2.505 g of methyl-2-isocyanato-3-methylbutylrate were mixed together and heated to ~98°C. Films were casted onto two separate glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes, respectively. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 38

5.980 g of the Carboset XPD2470/DMF solution, 2.500 g of acrylamide and 2.518 g of triallyl isocyanurate were mixed together and melted at ~95°C. Films were casted on glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 39

5.974 g of the Carboset XPD2470/DMF solution, 2.498 g of acrylamide and 2.503 g of triglycidal isocyanurate were mixed together and heated to ~140°C. Films were casted onto two separate glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 40

5.984 g of the Carboset XPD2470/DMF solution, 2.510 g of acrylamide and 2.509 g of tris(2-acryloxyethyl) isocyanurate were mixed together and heated to ~100°C. Films were casted onto two glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes, respectively. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 41

2.394 g of the Carboset XPD2470/DMF solution, 0.998 g of PEGDMA and 0.998 g of urea were mixed together and heated to ~131°C. Films were casted onto two separate glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes, respectively. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 42

2.394 g of the Carboset XPD2470/DMF solution, 0.996 g of PEGDMA and 1.004 g of urethane were mixed together and heated to ~85°C. Films were casted onto two separate glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes, respectively. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 43

2.386 g of the Carboset XPD2470/DMF solution, 1.000 g of PEGDMA and 0.997 g of butylcarbamate were mixed together and heated to ~85°C. Films were casted on glass substrates. The films were irradiated by a x-ray beam from a Mo target for 10 and 30 minutes. Both gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 44

5.298 g of the Carboset XPD2470/DMF solution, 2.646 g of acrylamide and 1.775 g of PEGDMA were mixed together and stirred at room temperature for 2 hours, then 6.203 g of silica glass particles (71% SiO₂, 26% B₂O₃, 0.5% Na₂O, 1% K₂O, 1% Al₂O₃, 0.5% LiO) was added and the mixture was stirred for ~30 minutes. Three films were casted onto separate glass substrates from the mixture using a 30 mil doctor knife. After air drying the first film for 1.5 hours, second and third layers were casted and air dried overnight. The films were irradiated by a x-ray beam from a Mo target for 10, 20 and 30 minutes. All gave positive results once developed with acetone. An insoluble spot was formed where the x-ray beam irradiated.

EXAMPLE 45

2.995 g of acrylamide was melted at ~85°C. Then 0.745 g of BiI₃ was added to the clear melt and the resulting orange-brown mixture was stirred for 5 minutes. The melt was casted onto two glass substrates to form films. The films were irradiated with a x-ray beam from a Mo target for 10 and 30 minutes, respectively. The films were then developed by washing with acetone. Insoluble spots were formed where the x-ray beam irradiated.

COMPARATIVE EXAMPLE E

1.436 g of Poly(acrylic acid) was loaded into a 1.5 cm glass vial. The sample was irradiated by a x-ray beam from Mo target for 1 hour. No insoluble product was formed and no image was developed. This example demonstrates that poly(acrylic acid) alone is not effective.

EXAMPLE 46

2.395 g of acrylamide, 1.618 g of acrylic acid and 5.010 g of Carboset XPD2470/DMF solution (20% solids) were mixed together and heated to ~85°C. A vial of 1.5 cm diameter was filled with the mixture. The vial was irradiated by a x-ray beam from a Mo target for 60 minutes. The contents of the vial were developed by washing with acetone. A solid white plug, a replica of the x-ray beam, was formed in the vial sample.

EXAMPLE 47

3.002 g of acrylamide and 2.999 g of poly(acrylic acid) were mixed together and melted at ~85°C. A vial (1.5 cm diameter) was filled with the melt. The vial was irradiated by a x-ray beam from a Mo target for 60 minutes. The contents of the vial were developed by washing with acetone. A solid white plug, a replica of the x-ray beam, was formed in the vial sample.

EXAMPLE 48

2.509 g of Carboset XPD2470/DMF solution (20 wt. % solids), 1.208 g of N-(iso-butoxy-methyl)acrylamide and 0.807 g of PEGDMA were mixed together and heated to ~100°C. A glass vial was filled with the mixtures. The vial was irradiated by a x-ray beam from a Mo target for 30 minutes. The irradiated vial was washed with acetone. A solid white plug, a replica of the x-ray beam, was formed in the vial sample.

EXAMPLE 49

2.501 g of Carboset XPD2470/DMF solution (20 wt. % solids), 1.201 g of acrylamide and 0.803 g of 1,4-butanedioldimethacrylate were mixed together and heated to ~80°C. Filled a glass vial with the mixtures. The vial was irradiated by a x-ray beam from a Mo target for 30 minutes. The irradiated vial was washed with acetone. A solid white plug, a replica of the x-ray beam, was formed in the vial sample.

EXAMPLE 50

2.512 g of Carboset XPD2470/DMF solution (20% solids), 1.201 g of acrylamide and 0.803 g of poly(propylene glycol)_{M.W. ~300} monoethacrylate were mixed together and heated to ~80°C. Filled a glass vial with the mixtures. The vial was irradiated by a x-ray beam from a Mo target for 30 minutes. The irradiated vial was washed with acetone. A clear soft plug, a replica of the x-ray beam, was formed in the vial sample.

EXAMPLE 51

2.506 g of Carboset XPD2470/DMF solution (20 wt. % solids), 1.202 g of acrylamide and 0.820 g of poly(propyleneoxide)cyclocarbonate terminated were mixed together and heated to ~80°C. A glass vial was filled with the mixtures.

The vial was irradiated by a x-ray beam from a Mo target for 30 minutes. The irradiated vial was washed with acetone. A solid white plug, a replica of the x-ray beam, was formed in the vial sample.

EXAMPLE 52

5 2.504 g of Carboset XPD2470/DMF solution (20 wt. % solids), 1.199 g of acrylamide and 0.820 g of poly(propyleneoxide) epoxy were mixed together and heated at ~120°C. A glass vial was filled with the mixtures. The vial was irradiated by a x-ray beam from a Mo target for 30 minutes. The irradiated vial was washed with acetone. A solid white plug, a replica of the x-ray beam, was
10 formed in the vial sample.

EXAMPLE 53

2.508 g of Carboset XPD2470/DMF solution (20 wt. % solids), 1.202 g of acrylamide and 0.813 g of triethylene glycol diacrylate were mixed together and heated to ~80°C. A glass vial was filled with the mixtures. The vial was irradiated
15 by a x-ray beam from a Mo target for 30 minutes. The irradiated vial was washed with acetone. A solid white plug, a replica of the x-ray beam, was formed in the vial sample.

EXAMPLE 54

2.520 g of Carboset XPD2470/DMF solution (20 wt. % solids), 1.197 g of
20 acrylamide and 0.811 g of triglycidal isocyanurate were mixed together and heated at ~120°C. A glass vial was filled with the mixtures. The vial was irradiated by a x-ray beam from a Mo target for 30 minutes. The irradiated vial was washed with acetone. A solid white plug, a replica of the x-ray beam, was formed in the vial sample.

EXAMPLE 55

25 5.977 g of Carboset XPD2470/DMF (20 wt. %) solution, 2.502 g of acrylamide and 2.513 g of triethylene glycol diacrylate were mixed together and heated to ~100°C, at which time a clear homogeneous solution was formed. A glass vial was filled with some of the solution. The vial was irradiated by a x-ray
30 beam from a Mo target for 30 minutes. A solid white material was formed. Rinsed with acetone to develop.

EXAMPLE 56

5.974 g of Carboset XPD2470/DMF (20 wt. %) solution, 2.509 g of
acrylamide and 2.511 g of tri-glycidyl isocyanurate were mixed together and
35 heated to ~155°C, at which time a thick cloudy solution was formed. A glass vial was filled with some of the solution. The vial was irradiated by a x-ray beam from a Mo target for 30 minutes. A solid white plug was observed. Rinsed with acetone to develop.

EXAMPLE 57

2.499 g of Carboset XPD2470/DMF (20 wt. %) solution, 1.199 g of n-allyl acrylamide and 0.799 g of PEGDMA were mixed together and heated to ~105°C, at which time the mixture was a cloudy tea-colored and full of tiny bubbles. A glass vial was filled with some of the solution. The vial was irradiated by a x-ray beam from a Mo target for 60 minutes. The contents of the vial were rinsed with acetone to develop. A small tea-colored mass was formed on the wall of the vial.

EXAMPLE 58

2.502 g of Carboset XPD2470/DMF (20 wt. %) solution, 1.202 g of n-(iso-butoxymethyl)methyl-acrylamide and 0.807 g of PEGDMA were mixed together and heated to ~95°C, at which time the mixture was clear and homogeneous. A glass vial was filled with some of the solution. The vial was irradiated by a x-ray beam from a Mo target for 60 minutes and developed with acetone. A clear gel that spanned halfway across the diameter of the vial was formed.

EXAMPLE 59

2.497 g of Carboset XPD2470/DMF (20 wt. %) solution, 1.204 g of malonamide and 0.806 g of PEGDMA were mixed together and heated to ~175°C, at which time the mixture was cloudy and white with no sign of insolubles. A glass vial was filled with some of the solution. The vial was irradiated by a x-ray beam from a Mo target for 60 minutes and developed with acetone. A white plug which spanned halfway across the diameter of the vial was formed.

EXAMPLE 60

Added to 5.018 g of poly(vinylacetate)/DMF solution (20 wt. % solids), 2.408 g of acrylamide and 1.604 g of PEGDMA. The mixture was stirred at room temperature for ~1.5 hours, after which time the mixture was clear, homogeneous, and very viscous. Two microscope slides were coated with the solution. Two glass vials were also filled with some of the solution. The vials were irradiated immediately by a x-ray beam from a Mo target for 10 and 30 minutes, respectively, and then developed with acetone. A small white mass was formed on the wall of the vial that was irradiated for 10 minutes while a white plug was formed across the diameter of the 30 minute vial. The slides were air dried at room temperature overnight then irradiated under the same conditions as the vials for 10 and 30 minutes. Developed with acetone and observed positive results in both cases as insoluble dots formed.

EXAMPLE 61

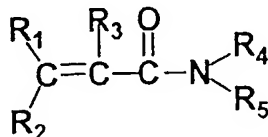
Added to 2.518 g of XPD2470/DMF solution (20 wt. % solids), 1.015 g of acrylamide and 1.001 g of PEGDMA. The mixture was heated to ~85°C, at which

time the mixture became clear and homogeneous. Several microscope slides were coated with the solution and air dried at room temperature overnight. A slide was irradiated using the 2 and 4 LP/mm area of a Pb mask with a x-ray beam from a Mo target for 8 minutes, and developed with acetone. Insoluble line patterns, corresponding to the image of the Pb mask, were formed on the slide after developing. Micrograph from a 4 LP/mm mask is shown in Fig. 4 where the line width is about 140 microns.

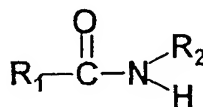
What is claimed is:

1. A composition, that can be polymerized/cross-linked imagewise by ionizing radiation, consisting essentially of:

- (A) from 10 to 90 weight percent of a reactive monomer having at least one amide functional group, said monomer selected from the group consisting of:



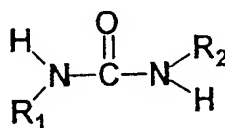
- where R_1 , R_2 , R_3 , R_4 , and R_5 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, and aliphatic groups with $R'O-$ substituent where R' represents aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);



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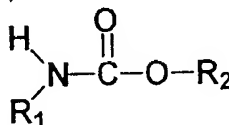
where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and acetamide;

20



- where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20);

25



- where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and amino-substituted aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

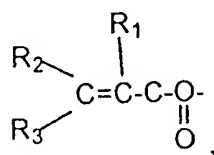
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(B) from 10 to 90 weight percent of a multifunctional cross-linking agent, said cross-linking agent consists of a backbone having at least 2 functional groups, said backbone is selected from the group consisting of:

- (1) linear or branched aliphatic chains, $-(CRH)_n-$, $n=1-1000$, where R represents an aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);
- (2) ethylene glycol chains, $-(CH_2CH_2O)_n-$ where $n=1-1000$;
- (3) propylene glycol chains, $-(CH(CH_3)CH_2O)_n-$ where $n=1-1000$;
- (4) cyclohexyl; and
- (5) isocyanurate, $C_3N_3O_3$; and

wherein the functional groups are selected from the group consisting of:

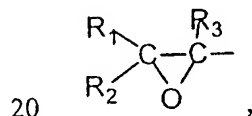
(a) acrylates,



where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

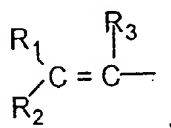
(b) carboxylic acid, $-COOH$;

(c) epoxides,



where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and

(d) vinyls,



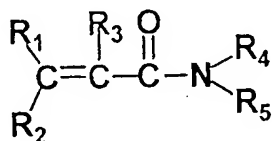
where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and

(C) from 0.1 to 80 weight percent of an inorganic radiation sensitizer having a particle size in the range of 1 nanometer to 1000 nanometers, said radiation sensitizer is selected from the group consisting of VB-VIB semiconductors, VB-VIIB semiconductors, IIB-VIB semiconductors, IIB-VB

semiconductors, IIIB-VB semiconductors, IIIB-VIB semiconductors, IB-VIB semiconductors, and IVB-VIIB semiconductors.

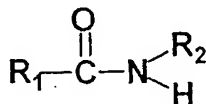
2. A composition, that can be polymerized/cross-linked imagewise by ionizing radiation, consisting essentially of:

- 5 (A) from 10 to 90 weight percent of a reactive monomer having at least one amide functional group, said monomer selected from the group consisting of:

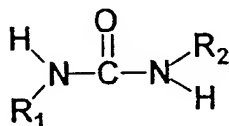


- 10 where R_1 , R_2 , R_3 , R_4 , and R_5 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, and aliphatic groups with $R'O-$ substituent where R' represents aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

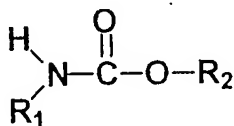
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- where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and acetamide;
- 20



- where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20);
- 25



- 30 where R_1 and R_2 are selected from the group consisting of: hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and amino-substituted aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to

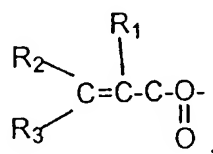
20);

(B) from 10 to 90 weight percent of a multifunctional cross-linking agent, said cross-linking agent consists of a backbone having at least 2 functional groups, said backbone is selected from the group consisting of:

- 5 (1) linear or branched aliphatic chains, $-(CRH)_n-$, $n=1-1000$, where R represents an aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);
 (2) ethylene glycol chains, $-(CH_2CH_2O)_n-$ where $n=1-1000$;
 (3) propylene glycol chains, $-(CH(CH_3)CH_2O)_n-$ where $n=1-1000$;
 (4) cyclohexyl; and
 10 (5) isocyanurate, $C_3N_3O_3$; and

wherein the functional groups are selected from the group consisting of:

(a) acrylates,



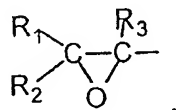
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where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

(b) carboxylic acid, $-COOH$;

(c) epoxides,

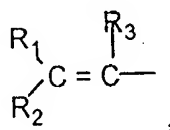
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where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and

25

(d) vinyls,



where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

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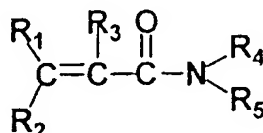
(C) from 0.1 to 80 weight percent of an inorganic radiation sensitizer having a particle size in the range of 1 nanometer to 1000 nanometers, said radiation sensitizer is selected from the group consisting of VB-VIB

semiconductors, VB-VIIB semiconductors, IIB-VIB semiconductors, IIB-VB semiconductors, IIIB-VB semiconductors, IIIB-VIB semiconductors, IB-VIB semiconductors, and IVB-VIIB semiconductors; and

(D) 5 to 90 weight percent of a polymer binder.

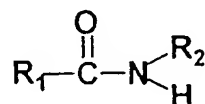
- 5 3. A composition, that can be polymerized/cross-linked imagewise by ionizing radiation, consisting essentially of:

(A) from 10 to 90 weight percent of a reactive monomer having at least one amide functional group, said monomer selected from the group consisting of:

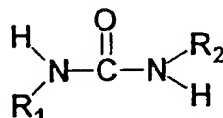


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where R_1 , R_2 , R_3 , R_4 , and R_5 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, and
 15 aliphatic groups with $R'O$ - substituent where R' represents aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

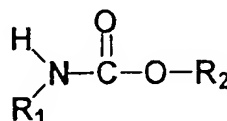


- 20 where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and acetamide;



25

where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20);



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where R_1 and R_2 are selected from the group consisting of: hydrogen; aliphatic

groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and amino-substituted aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

- (B) from 10 to 90 weight percent of a multifunctional cross-linking agent, said cross-linking agent consists of a backbone having at least 2 functional groups, said backbone is selected from the group consisting of:

(1) linear or branched aliphatic chains, $-(CRH)_n-$, $n=1-1000$, where R represents an aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

(2) ethylene glycol chains, $-(CH_2CH_2O)_n-$ where $n=1-1000$;

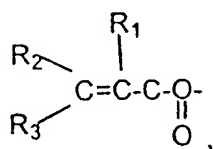
(3) propylene glycol chains, $-(CH(CH_3)CH_2O)_n-$ where $n=1-1000$;

(4) cyclohexyl; and

(5) isocyanurate, $C_3N_3O_3$; and

wherein the functional groups are selected from the group consisting of:

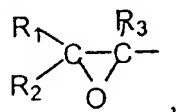
(a) acrylates,



where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

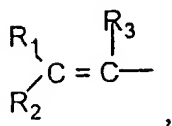
(b) carboxylic acid, $-COOH$;

(c) epoxides,



- where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and

(d) vinyls,

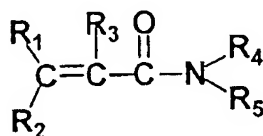


where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

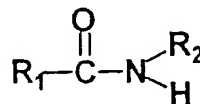
- (C) from 0.1 to 80 weight percent of an inorganic radiation sensitizer having a particle size in the range of 1 nanometer to 1000 nanometers, said radiation sensitizer is selected from the group consisting of VB-VIB semiconductors, VB-VIIB semiconductors, IIB-VIB semiconductors, IIB-VB semiconductors, IIIB-VB semiconductors, IIIB-VIB semiconductors, IB-VIB semiconductors, and IVB-VIIB semiconductors;
- (D) 5 to 90 weight percent of a polymer binder; and
- (E) 5 to 90 weight percent of metallic particle or ceramic oxide fillers, said metallic filler is selected from group consisting of Al, Ti, V, Cu, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, In, and Sb; said oxide filler is selected from the group consisting of Al, Ti, V, Cu, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, In, Sb, Ta, W, and Si.

4. A composition, that can be polymerized/cross-linked imagewise by ionizing radiation, consisting essentially of:

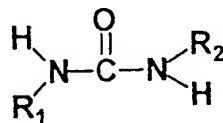
- (A) from 10 to 90 weight percent of a reactive monomer having at least one amide functional group, said monomer selected from the group consisting of:



- where R_1 , R_2 , R_3 , R_4 , and R_5 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, and aliphatic groups with $R'O-$ substituent where R' represents aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

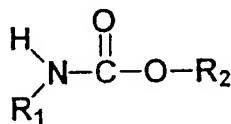


- where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and acetamide;



where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic

groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20);



5

where R_1 and R_2 are selected from the group consisting of: hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and amino-substituted aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

10

(B) from 10 to 90 weight percent of a multifunctional cross-linking agent, said cross-linking agent consists of a backbone having at least 2 functional groups, said backbone is selected from the group consisting of:

(1) linear or branched aliphatic chains, $-(CRH)_n-$, $n=1-1000$, where R represents an aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

15

(2) ethylene glycol chains, $-(CH_2CH_2O)_n-$ where $n=1-1000$;

(3) propylene glycol chains, $-(CH(CH_3)CH_2O)_n-$ where $n=1-1000$;

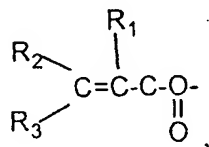
(4) cyclohexyl; and

(5) isocyanurate, $C_3N_3O_3$; and

wherein the functional groups are selected from the group consisting of:

20

(a) acrylates,

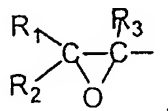


where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

25

(b) carboxylic acid, $-\text{COOH}$;

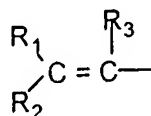
(c) epoxides,



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where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and

(d) vinyls,

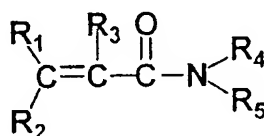


- 5 where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and

(C) 5-90 weight percent of a polymer binder.

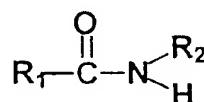
5. A composition, that can be polymerized/cross-linked imagewise by ionizing radiation, consisting essentially of:

- 10 (A) from 10 to 90 weight percent of a reactive monomer having at least one amide functional group, said monomer selected from the group consisting of:



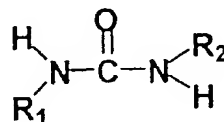
- 15 where R_1 , R_2 , R_3 , R_4 , and R_5 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); aliphatic groups with amide or acrylamide substituent, and aliphatic groups with $R'O-$ substituent where R' represents aliphatic group, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

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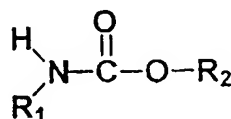
where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20); and acetamide;

25



where R_1 and R_2 are selected from the group consisting of hydrogen; aliphatic groups C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20); and unsaturated aliphatic groups C_nH_{2n-1} ($n=1$ to 20);

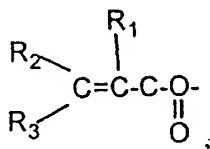
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where R_1 and R_2 are selected from the group consisting of: hydrogen; aliphatic groups $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$ ($n=1$ to 20); unsaturated aliphatic groups $\text{C}_n\text{H}_{2n-1}$ ($n=1$ to 20); and amino-substituted aliphatic groups, $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$ ($n=1$ to 20);

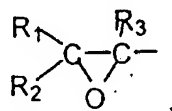
(B) from 10 to 90 weight percent of a multifunctional cross-linking agent, said cross-linking agent consists of a backbone having at least 2 functional groups, said backbone selected from the group consisting of:

- (1) linear or branched aliphatic chains, $-(\text{CRH})_n-$, $n=1-1000$, where R represents an aliphatic group, $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$ ($n=1$ to 20);
- (2) ethylene glycol chains, $-(\text{CH}_2\text{CH}_2\text{O})_n-$ where $n=1-1000$;
- (3) propylene glycol chains, $-(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_n-$ where $n=1-1000$;
- (4) cyclohexyl; and
- (5) isocyanurate, $\text{C}_3\text{N}_3\text{O}_3$; and wherein the functional groups are selected from the group consisting of:
 - (a) acrylates,



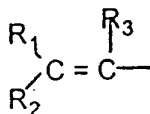
where R_1 , R_2 , and R_3 are selected from the group consisting of hydrogen and aliphatic groups, $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$ ($n=1$ to 20);

- (b) carboxylic acid, $-\text{COOH}$;
- (c) epoxides,



where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, $\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}$ ($n=1$ to 20); and

(d) vinyls,



5 where R_1 , R_2 , and R_3 are selected from: hydrogen or aliphatic groups, C_nH_{2n+1} and C_nH_{2n-1} ($n=1$ to 20);

(C) 5 to 90 weight percent of a polymer binder; and

(D) 5 to 90 weight percent of metallic or oxide fillers, said metallic filler is selected from group consisting of Al, Ti, V, Cu, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, In, and Sb; said oxide filler is selected from the group consisting of Al, Ti, V, Cu, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, In, Sb, Ta, W, and Si.

6. The composition of Claim 1, 2, 3, 4 or 5 wherein the reactive monomer is selected from the group consisting of acrylamide, methylacrylamide, N-(t-butyl) acrylamide, acetamide, N-cyclohexylacrylamide, N-(3-aminopropyl)-methacrylamide, urea, urethane, butylcarbamate, N,N'-methylenbisacrylamide, N-allylacrylamide, N-(iso-butoxymethyl)methylacrylamide, and malonamide.

7. The composition of Claim 1, 2, 3, 4 or 5 wherein the multi-functional cross-linking agent is selected from the group consisting of: itaconic acid, malonic acid, polyacrylic acid, 1,4-cyclohexanediol dimethylacrylate, allylmethacrylate, poly(ethyleneglycol)dimethylacrylate, poly(ethylene-glycol)diacrylate, poly(ethyleneglycol)diglycidyl ether, 3-butene-1,2,3-tricarboxylic acid, 1,1,1-trimethylolpropane trimethacrylate, methyl-2-isocyanato-3-methylbutyrate, triallylisocyanurate, tris(2-acryloxyethyl)isocyanurate, triethylene glycol diacrylate, and tris(2,3-epoxypropyl)isocyanurate.

8. The composition of Claim 1, 2 or 3 wherein the radiation sensitizer is selected from the group consisting of: Bi_2S_3 , Bi_2Se_3 , BiI_3 , $BiBr_3$, HgS , PbI_2 , $[PbI_4]^{-2}$, and $[Pb_2I_7]^{-3}$.

9. The composition of Claim 1, 2, 3, 4 or 5 wherein the reactive monomer is selected from the group consisting of acrylamide, methylacrylamide, N-(t-butyl)acrylamide, acetamide, N-cyclohexylacrylamide, N-(3-aminopropyl)-methacrylamide, urea, urethane, butylcarbamate, N,N'-methylenbisacrylamide, N-allylacrylamide, N-(iso-butoxymethyl)methylacrylamide, and malonamide; and wherein the multi-functional cross-linking agent is selected from the group consisting of itaconic acid, malonic acid, polyacrylic acid, 1,4-cyclohexanediol dimethylacrylate, allylmethacrylate, poly(ethyleneglycol)dimethylacrylate, poly(ethylene-glycol)diacrylate, poly(ethyleneglycol)diglycidyl ether, 3-butene-1,2,3-tricarboxylic acid, 1,1,1-trimethylolpropane trimethacrylate, methyl-2-

isocyanato-3-methylbutyrate, triallylisocyanurate, tris(2-acryloxyethyl)-isocyanurate, triethylene glycol diacrylate, and tris(2,3-epoxypropyl)isocyanurate.

10. The composition of Claim 1, 2, or 3 wherein the reactive monomer is selected from the group consisting of acrylamide, methylacrylamide, N-(t-butyl)acrylamide, acetamide, N-cyclohexylacrylamide, N-(3-aminopropyl)-methacrylamide, urea, urethane, butylcarbamate, N,N'-methylenebisacrylamide, N-allylacrylamide, N-(iso-butoxymethyl)methylacrylamide, and malonamide; wherein the multi-functional cross-linking agent is selected from the group consisting of itaconic acid, malonic acid, polyacrylic acid, 1,4-cyclohexanediol dimethylacrylate, allylmethacrylate, poly(ethyleneglycol)dimethylacrylate, poly(ethyleneglycol)diacrylate, poly(ethyleneglycol)diglycidyl ether, 3-butene-1,2,3-tricarboxylic acid, 1,1,1-trimethylolpropane trimethacrylate, methyl-2-isocyanato-3-methylbutyrate, triallylisocyanurate, tris(2-acryloxyethyl)-isocyanurate, triethylene glycol diacrylate, and tris(2,3-epoxypropyl)isocyanurate; and wherein the radiation sensitizer is selected from the group consisting of Bi_2S_3 , Bi_2Se_3 , BiI_3 , BiBr_3 , HgS , PbI_2 , $[\text{PbI}_4]^{-2}$, and $[\text{Pb}_2\text{I}_7]^{-3}$.

11. The composition of Claim 2 or 3 wherein the reactive monomer is selected from the group consisting of acrylamide, methylacrylamide, N-(t-butyl)acrylamide, acetamide, N-cyclohexylacrylamide, N-(3-aminopropyl)-methacrylamide, urea, urethane, butylcarbamate, N,N'-methylenebisacrylamide, N-allylacrylamide, N-(iso-butoxymethyl)methylacrylamide, and malonamide; wherein the multi-functional cross-linking agent is selected from the group consisting of: itaconic acid, malonic acid, polyacrylic acid, 1,4-cyclohexanediol dimethylacrylate, allylmethacrylate, poly(ethyleneglycol)dimethylacrylate, poly(ethyleneglycol)diacrylate, poly(ethyleneglycol)diglycidyl ether, 3-butene-1,2,3-tricarboxylic acid, 1,1,1-trimethylolpropane trimethacrylate, methyl-2-isocyanato-3-methylbutyrate, triallylisocyanurate, tris(2-acryloxyethyl)-isocyanurate, triethylene glycol diacrylate, and tris(2,3-epoxypropyl)isocyanurate; wherein the polymer binder is selected from the group consisting of acrylate polymers, acrylate-acrylic acid copolymers, epoxy polymers, polyamides, polyacrylamides, polyvinylalcohol, poly(ethylene)glycol, poly(propylene)glycol, polyethylene, and polyvinylacetate; and wherein the sensitizer is selected from the group consisting of: Bi_2S_3 , Bi_2Se_3 , BiI_3 , BiBr_3 , HgS , PbI_2 , $[\text{PbI}_4]^{-2}$, and $[\text{Pb}_2\text{I}_7]^{-3}$.

12. The composition of Claim 2, 3, 4 or 5 wherein the reactive monomer is selected from the group consisting of acrylamide, methylacrylamide, N-(t-butyl)acrylamide, acetamide, N-cyclohexylacrylamide, N-(3-aminopropyl)-methacrylamide, urea, urethane, butylcarbamate, N,N'-methylenebisacrylamide,

N-allylacrylamide, N-(iso-butoxymethyl)methylacrylamide, and malonamide; wherein the multi-functional cross-linking agent is selected from the group consisting of itaconic acid, malonic acid, polyacrylic acid, 1,4-cyclohexanediol dimethylacrylate, allylmethacrylate, poly(ethyleneglycol)dimethylacrylate, poly(ethyleneglycol)diacrylate, poly(ethyleneglycol)diglycidyl ether, 3-butene-1,2,3-tricarboxylic acid, 1,1,1-trimethylolpropane trimethacrylate, methyl-2-isocyanato-3-methylbutyrate, triallylisocyanurate, tris(2-acryloxyethyl)-isocyanurate, triethylene glycol diacrylate, and tris(2,3-epoxypropyl)isocyanurate; and wherein the polymer binder is selected from the group consisting of acrylate polymers, acrylate-acrylic acid copolymers, epoxy polymers, polyamides, polyacrylamides, polyvinylalcohol, poly(ethylene)glycol, poly(propylene)glycol, polyethylene, and polyvinylacetate.

13. The compositions of Claim 2, 3, 4 or 5 wherein the polymer binder is selected from the group consisting of acrylate polymers, acrylate-acrylic acid copolymers, epoxy polymers, polyamides, polyacrylamides, polyvinylalcohol, poly(ethylene)glycol, poly(propylene)glycol, polyethylene, and polyvinylacetate.

14. The composition of Claim 3 wherein the reactive monomer is selected from the group consisting of acrylamide, methylacrylamide, N-(t-butyl)-acrylamide, acetamide, N-cyclohexylacrylamide, N-(3-aminopropyl)-methacrylamide, urea, urethane, butylcarbamate, N,N'-methylenabisacrylamide, N-allylacrylamide, N-(iso-butoxymethyl)methylacrylamide, and malonamide; wherein the multi-functional cross-linking agent is selected from the group consisting of itaconic acid, malonic acid, polyacrylic acid, 1,4-cyclohexanediol dimethylacrylate, allylmethacrylate, poly(ethyleneglycol)dimethylacrylate, poly(ethyleneglycol)diacrylate, poly(ethyleneglycol)diglycidyl ether, 3-butene-1,2,3-tricarboxylic acid, 1,1,1-trimethylolpropane trimethacrylate, methyl-2-isocyanato-3-methylbutyrate, triallylisocyanurate, tris(2-acryloxyethyl)-isocyanurate, triethylene glycol diacrylate, and tris(2,3-epoxypropyl)isocyanurate; wherein the polymer binder is selected from the group consisting of acrylate polymers, acrylate-acrylic acid copolymers, epoxy polymers, polyamides, polyacrylamides, polyvinylalcohol, poly(ethylene)glycol, poly(propylene)glycol, polyethylene, and polyvinylacetate; wherein the filler is selected from the group consisting of aluminum, aluminum oxide, and silicon oxide; and wherein the sensitizer is selected from the group consisting of Bi_2S_3 , Bi_2Se_3 , BiI_3 , BiBr_3 , HgS , PbI_2 , $[\text{PbI}_4]^{-2}$, and $[\text{Pb}_2\text{I}_7]^{-3}$.

15. The composition of Claim 3 or 5 wherein the reactive monomer is selected from the group consisting of acrylamide, methylacrylamide, N-(t-butyl)acrylamide, acetamide, N-cyclohexylacrylamide, N-(3-aminopropyl)-

methacrylamide, urea, urethane, butylcarbamate, N,N'-methylenebisacrylamide, N-allylacrylamide, N-(iso-butoxymethyl)methylacrylamide, and malonamide; wherein the multi-functional cross-linking agent is selected from the group consisting of itaconic acid, malonic acid, polyacrylic acid, 1,4-cyclohexanediol dimethylacrylate, allylmethacrylate, poly(ethyleneglycol)dimethylacrylate, 5 poly(ethyleneglycol)diacrylate, poly(ethyleneglycol)diglycidyl ether, 3-butene-1,2,3-tricarboxylic acid, 1,1,1-trimethylolpropane trimethacrylate, methyl-2-isocyanato-3-methylbutyrate, triallylisocyanurate, tris(2-acryloxyethyl)-isocyanurate, triethylene glycol diacrylate, and tris(2,3-epoxypropyl)isocyanurate; 10 and wherein the filler is selected from the group consisting of aluminum, aluminum oxide, and silicon oxide.

16. The composition of Claim 3 or 5 wherein the reactive monomer is selected from the group consisting of acrylamide, methylacrylamide, N-(t-butyl)acrylamide, acetamide, N-cyclohexylacrylamide, N-(3-aminopropyl)- 15 methacrylamide, urea, urethane, butylcarbamate, N,N'-methylenebisacrylamide, N-allylacrylamide, N-(iso-butoxymethyl)methylacrylamide, and malonamide; wherein the multi-functional cross-linking agent is selected from the group consisting of itaconic acid, malonic acid, polyacrylic acid, 1,4-cyclohexanediol dimethylacrylate, allylmethacrylate, poly(ethyleneglycol)dimethylacrylate, 20 poly(ethyleneglycol)diacrylate, poly(ethyleneglycol)diglycidyl ether, 3-butene-1,2,3-tricarboxylic acid, 1,1,1-trimethylolpropane trimethacrylate, methyl-2-isocyanato-3-methylbutyrate, triallylisocyanurate, tris(2-acryloxyethyl)-isocyanurate, triethylene glycol diacrylate, and tris(2,3-epoxypropyl)isocyanurate; 25 wherein the polymer binder is selected from the group consisting of acrylate polymers, acrylate-acrylic acid copolymers, epoxy polymers, polyamides, polyacrylamides, polyvinylalcohol, poly(ethylene)glycol, poly(propylene)glycol, polyethylene, and polyvinylacetate; and wherein the filler is selected from the group consisting of aluminum, aluminum oxide, and silicon oxide.

17. The composition of Claim 3 or 5 wherein the filler is selected from the 30 group consisting of aluminum, aluminum oxide, and silicon oxide.

18. The composition of Claim 3 or 5 wherein in polymer binder is selected from the group consisting of acrylate polymers, acrylate-acrylic acid copolymers, epoxy polymers, polyamides, polyacrylamides, polyvinylalcohol, poly(ethylene)-glycol, poly(propylene)glycol, polyethylene, and polyvinylacetate; and wherein the 35 filler is selected from the group consisting of aluminum, aluminum oxide, and silicon oxide.

19. A method of microfabricating ceramic or metal patterns on a solid substrate using ionization radiation comprising the steps of:

mixing together a composition consisting essentially of a reactive monomer, a multi-functional cross-linking agent and filler; said mixing process optionally carried out either by heating the composition until melted or by dissolving components in a common solvent;

5 optionally, in the presence of binder; and
optionally, in the presence of a radiation sensitizer;
casting the composition on a solid substrate to form a film of desired thickness;

10 irradiating the film with ionization radiation through a mask to form a polymerized/cross-linked image;

developing the polymerized/cross-linked image by rinsing the irradiated film in a solvent to remove unirradiated composition; and

sintering the polymerized/cross-linked image in microfabricated ceramics or metal patterns.

15 20. The method of Claim 19 wherein the composition is selected from the group consisting of the compositions of Claim 3 or Claim 5.

21. The method of Claim 19 wherein the source of ionizing radiation is selected from the group consisting of x-ray, electron beam and gamma ray.

22. The method of Claim 19 wherein the solid substrate is glass.

20 23. A method of performing lithography on a semiconductor surface using ionization radiation, comprising the steps of:

mixing together a composition consisting essentially of a reactive monomer and a multi-functional cross-linking agent, optionally by heating the composition until melted or by dissolving in a common solvent;

25 optionally, in the presence of a polymer binder; and
optionally, in the presence of a radiation sensitizer;
casting the composition on a solid substrate to form a film of desired thickness;

30 irradiating the film with ionization radiation through a mask to form a polymerized/cross-linked image;

developing the polymerized/cross-linked image by rinsing the irradiated film in a solvent to remove unirradiated composition.

35 24. The method of Claim 23 wherein an exposed semiconductor surface is subjected to etching and doping while the polymerized/cross-linked region of the film is protected from etching and doping.

25. The method of Claim 23 wherein the composition is selected from the group consisting of the compositions of Claim 1, 2 or 4.

26. The method of Claim 23 wherein the ionization radiation is selected from the group consisting of x-ray, electron beam, gamma ray, and ion beam.
27. The method of Claim 23 wherein the solid substrate is glass.
28. A method of forming a three-dimensional solid object of polymers, ceramics, or metals using ionization radiation, comprising the steps of:
- 5 mixing together a composition consisting essentially of a reactive monomer, a multi-functional cross-linking agent, and a polymer binder, said mixing process optionally done by dissolving in a common solvent or by pouring the composition into a container with a target substrate immersed in it;
- 10 optionally, in the presence of a radiation sensitizer; and
optionally, in the presence of a metallic or oxide filler;
irradiating the composition with ionization radiation through a mask or a focused source of ionization radiation to deposit a layer of material on the targeted substrate;
- 15 stepping back the substrate and irradiating the substrate;
repeating the step of stepping back the substrate and irradiating the substrate until a desired three-dimensional solid object is formed; and
optionally, treating the solid object post-irradiation.
29. The method of Claim 28 wherein the post-irradiation treatment is
- 20 sintering.
30. The method of Claim 28 wherein the composition is selected from the group consisting of the compositions of Claim 1, 2, 3, 4 or 5.
31. The method of Claim 30 wherein ionization radiation source is selected from the group consisting of x-ray and electron beam.

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INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 G03F7/027 G03F7/004 G03C9/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03F G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 489 467 A (TEIJIN LTD) 19 October 1977 (1977-10-19) examples 2-5	1-5
X	US 5 487 966 A (STEINMANN BETTINA ET AL) 30 January 1996 (1996-01-30) column 7, line 61 -column 8, line 10; table 1 column 8, line 23 - line 35	28
A	EP 0 414 169 A (DU PONT) 27 February 1991 (1991-02-27) the whole document	1-5
A	EP 0 414 168 A (DU PONT) 27 February 1991 (1991-02-27)	1-5
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 414 167 A (DU PONT) 27 February 1991 (1991-02-27) the whole document ---	1-5
A	EP 0 414 166 A (DU PONT) 27 February 1991 (1991-02-27) ---	1-5
A	US 5 556 716 A (HERRON NORMAN ET AL) 17 September 1996 (1996-09-17) cited in the application ---	1-3
A	US 4 115 339 A (RESTAINO ALFRED J) 19 September 1978 (1978-09-19) cited in the application claims ---	1-5
A	US 4 457 766 A (CAUL LAWRENCE D) 3 July 1984 (1984-07-03) cited in the application examples -----	1-5

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 99/23195

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1489467 A	19-10-1977	JP 924916 C	22-09-1978
		JP 50117502 A	13-09-1975
		JP 53002361 B	27-01-1978
		AU 7843075 A	26-08-1976
		BE 825793 A	16-06-1975
		DE 2507874 A	28-08-1975
		FR 2262328 A	19-09-1975
		NL 7502120 A	26-08-1975
US 5487966 A	30-01-1996	AT 132278 T	15-01-1996
		AU 653817 B	13-10-1994
		AU 1801292 A	10-12-1992
		CA 2070258 A	05-12-1992
		DE 59204801 D	08-02-1996
		EP 0517657 A	09-12-1992
		ES 2082425 T	16-03-1996
		JP 5249669 A	28-09-1993
EP 0414169 A	27-02-1991	US 5035980 A	30-07-1991
		AT 130109 T	15-11-1995
		CA 2023602 A	22-02-1991
		CN 1050448 A	03-04-1991
		DE 69023425 D	14-12-1995
		DE 69023425 T	04-04-1996
		JP 2680726 B	19-11-1997
		JP 3205461 A	06-09-1991
EP 0414168 A	27-02-1991	KR 9302937 B	15-04-1993
		US 5047313 A	10-09-1991
		AT 126365 T	15-08-1995
		CA 2023601 A	22-02-1991
		CN 1050268 A	27-03-1991
		DE 69021463 D	14-09-1995
		DE 69021463 T	22-02-1996
		JP 2095276 C	02-10-1996
EP 0414167 A	27-02-1991	JP 3205462 A	06-09-1991
		JP 8003057 B	17-01-1996
		US 5032490 A	16-07-1991
		AT 121551 T	15-05-1995
		CA 2023628 A	22-02-1991
		CN 1050447 A	03-04-1991
		DE 69018733 D	24-05-1995
		DE 69018733 T	09-11-1995
EP 0414166 A	27-02-1991	JP 1890553 C	07-12-1994
		JP 3210703 A	13-09-1991
		JP 6019925 B	16-03-1994
		US 5032478 A	16-07-1991
		AT 122478 T	15-05-1995
		CA 2023629 A	22-02-1991
		CN 1054495 A	11-09-1991
		DE 69019261 D	14-06-1995
		DE 69019261 T	09-11-1995
		JP 1890552 C	07-12-1994
		JP 3171690 A	25-07-1991
		JP 6019924 B	16-03-1994
		KR 9302936 B	15-04-1993

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/23195

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5556716 A	17-09-1996	DE 69512924 D EP 0777868 A WO 9606383 A	25-11-1999 11-06-1997 29-02-1996
US 4115339 A	19-09-1978	US 3926756 A	16-12-1975
US 4457766 A	03-07-1984	CA 1186276 A DE 3139813 A FR 2491377 A GB 2087263 A, B JP 57089565 A US 4547204 A US 4588419 A	30-04-1985 24-06-1982 09-04-1982 26-05-1982 03-06-1982 15-10-1985 13-05-1986